A

DISSERTATION REPORT

ON

A COMPARATIVE STUDY OF THE EFFECT OF REFINING ON FIBER CHARGE OF VARIOUS PULPS

Submitted for partial fulfillment of the requirements for the award of the degree of

MASTER OF TECHNOLOGY

IN

PULP AND PAPER TECHNOLOGY

Submitted by

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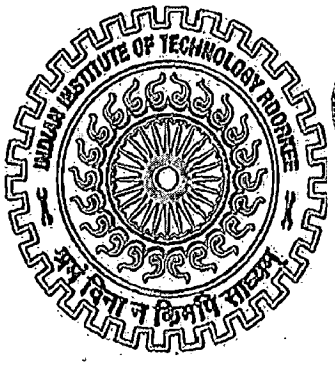

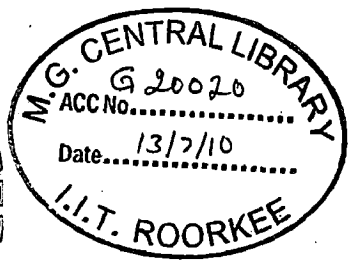

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JUNE - 2009

CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this Dissertation report, entitled **"A COMPARATIVE STUDY OF THE *EFFECT OF REFINING ON FIBER CHARGE OF VARIOUS PULPS*"** submitted for partial fulfillment of the requirements for the award of the degree of Master of Technology in Pulp and Paper Technology at IIT Roorkee, is an authentic record of my own work carried out, under the supervision of **Dr. *A. K. Ray,*** Professor & ***Dr. N. K. Bhardwaj,*** Assistant Professor, Department of Paper Technology, IIT Roorkee, Saharanpur Campus, Saharanpur. The matter presented in this Dissertation report has not been submitted by me for the award of any other degree of this or any other Institute.

Date: 30/06/09

Place: Saharanpur

Candidate's Signature

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ABSTRACT

The aim of this work was to study the influence of beating on various pulp properties such as freeness, specific surface area, Specific volume, surface charge and total charge. The beating operation is conducted in PFI mill with various revolutions at 10% consistency of the pulp. The results indicated that specific surface area and specific volume of the pulps as determined by permeability tester increased and increased with beating. The fibre surface charge, as determined by particle charge detector and titration with poly-DADMAC (Polydiallyldimethylammonium chloride), is also increased with beating. However, the total fibre charge, as determined by conductometric titration, is not affected by beating operation. It is also evident that increase in specific surface area of pulps by beating resulted in a higher fibre surface charge and also better fibre–fibre bonding.

Water retention value (WRV) is a measure of fibre flexibility and swelling. Water retention value (WRV) as determined by centrifuge method, increased with beating. The classification of fibres gives the amount of fines get drained through fibres as determined by Bauer Mcett fibre Classifier. Different paper properties are determined at different beating levels and how different pulps at various freeness levels affect the drainage was studied.

The experimental data are subjected to statistical analysis from graphs and then subjected to statistical regression analysis. Least square techniques have been used to develop some linear univariate regression models, which are found to be very accurate as the regression coefficients, R^2 are close to unity (on an average above 0.98) and the percentage error does not exceed in any case ± 7%. The comparison of model predicted data and the experimental data and also the comparison of residuals and model predicted value shows an excellent agreement between them. Therefore statistical predictions are claimed to be very good and reproducible with a reasonable degree of accuracy permitted in engineering estimates. Therefore the statistical regression can be used reliably for analysis purposes.

From the detailed analysis of data and their interpretation it can be certainly stated without any doubt that the surface area of fibres plays an important role in the bonding of the fibres. A large fibre surface area provided higher fibre surface charge and more areas for Fibre–Fibre contacts and, subsequently, more number of bonds is developed between fibres. The experimental results also showed strong linear correlations between the surface charge and the hand sheets properties.

ACKNOWLEDGEMENT

I would like to take this as an opportunity to express my profound sense of gratitude to my guides **Dr. A. K. Ray**, Professor and **Dr. N. K. Bhardwaj**, Assistant Professor, IIT Roorkee, Department of Paper Technology, Saharanpur campus, for inspiring me to enhance my knowledge by pursuing the innovative and challenging area of my Dissertation "A Comparative Studies on Effect of beating on fiber charge of various pulps". Their skillful guidance, keen interests, valuable suggestion and constant encouragement helped me during the Dissertation work.

I convey my sincere thanks to **Dr. S. P. Singh,** Associate Professor for his valuable guidance and for providing me Particle Charge Detector (PCD 02) to carry out this work.

I am very thankful to **Dr. Y. V. Sood**, Scientist-F & In charge SPPMC Division CPPRI and **Mr. Sanjay Tyagi** (Scientist), Central Pulp and Paper Research Institute (CPPRI) for their guidance and providing me the necessary required facilities in order to complete my Dissertation work.

My special thanks to **Mr. Karan singh, Mr. Raj kumar and Mr. J. P. Joshi**, Technicians, Central Pulp and Paper Research Institute (CPPRI) has helped me for completion of my Dissertation work.

I also express my gratitude to **Staff members**, department of paper technology has helped me for completion of my Dissertation work.

My special thanks to **Mr. Praveen Kumar, Mr. Pradeep Chowdhary and Mr. Shiv Kumar**, Ph.D Scholars for their support.

Date: 30/6/09

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NOMENCLATURE

O.D.	Oven Dry
A.D.	Air Dry
W.R.V.	Water Retention Value
GSM	gram per square meter
CSF	Canadian Standard Freeness
SW	Softwood
HW	Hardwood
ECF	Elemental Chlorine Free
TCF	Total Chlorine Free
CTMP	Chemi Thermo Mechanical Pulp
TMP	Thermo Mechanical Pulp
q	Specific charge density (mmol/kg)
Vp	Vol. of titrant used for pulp (ml)
Vb	Vol. of titrant used for blank (ml)
C	concentration of titrant (mol/l)
w	Solid content of pulp (g)
m:	Original sample are used for titration.
R_p	Specific resistance to permeation, cm/gm.
A	Pad area, cm^2
ΔP	Pressure drop, dynes/ cm^2
Q	Flow rate, cm^3/sec.
W	Pad weight, gm.
η	Viscosity, poises (gm./cm/sec.).
L	Pad thickness, cm.
K	Kozeny constant.
S_w	Pulp specific surface, cm^2/gm.
V	Pulp specific volume, cm^3/gm.
C	Pad density, gm/cm^3.
F	force, N (kg, lbf).
t	specimen thickness, m (cm, inch).
R^2	Regression coefficient

CHAPTER 1 INTRODUCTION

1.1 Introduction

Cellulosic fibres for papermaking are normally subjected to a mechanical treatment usually known as beating or refining. This treatment results in structural changes of the treated fibres, including fibre shortening and internal/external fibrillation [6, 24]. The physical changes of fibres during refining would make the fibre chemical components more accessible, and would affect the distribution of these components on the surface as well as within the laminated fibre wall [37]. The specific surface area and specific volume have been used to measure the primary effects caused by refining of pulps.

The cellulosic fibres normally carry a negative charge when suspended in water due to the presence of ionisable acidic groups in the hemicelluloses and lignin. The charge of fibres is a complex function of the chemical composition, state of ionization of the acid groups, and the nature and amount of additional substances adsorbed on the fibre surface. The population of ionisable groups depends on the origin of the fibres and on the chemical treatments such as pulping and bleaching. The characteristics of any particular fibre surface also depend greatly on the degree of mechanical treatment. In hardwoods the gluronoxylan concentrations in the outer secondary wall and the main secondary wall are slightly different, whereas in softwoods the content of glucuronoxylan, a main group of ionisable hemicelluloses, in the outer and inner secondary wall is much higher than in the main secondary wall [20]. For this reason the charge distributions on fibre surface and fibre wall are expected to change by modification of the fibre morphology. Although many methods have been developed for fibre charge measurement [28], titrations using a cationic polymer of high molecular weight are normally used to measure the charge on fibre surface [32].

Drainage has been studied mainly from hydrodynamic and mechanical point of view. Some of these studies are very fundamental and have led to or were associated with, the introduction of new technologies, such as twin wire forming and the replacement of table rolls by hydrofoils. The cellulosic nature of papermaking fibres and their interaction with water very much affect the drainage rate and the machine speed. Variations in drainage observed with pulp fibres are then interpreted in terms of their morphology and interaction with water. The fibre properties, which can be of some importance, are their shape, size and their mechanical properties all of these are influenced by interaction with water. The drainage

strongly depends upon density of fibre mat on wire and fibre properties including length, flexibility and degree of swelling [12].

Characterization of pulp slurries often involves measuring the drainage resistance. Drainage can be measured in static as well as in dynamic condition. The most common methods for drainage measurement in static condition are measurement of Canadian Standard Freeness (CSF) and Schopper Riegler(°SR). The testing result of both the methods strongly depends upon fines content and the compressibility of pulp. As smooth the drainage of fibres on wire part the machine runnability is higher, which reduces the vacuum consumption and eventually leads to the profit. On line drainage testing by "Dynamic Drainage Analyser", which is drainage measurement technique in dynamic condition, is more accurate method of measurement of drainage resistance of pulp slurries. The use of Dynamic Drainage Analyser is increasing along with adaption automatic control systems. DDA measures the pressure over the sheet as a function of dewatering time [16]. The batch devices are sensitive to temperature and consistency.

Water retention value is another method to measure drainage characteristic of pulp slurries. Water Retention Value (WRV) describes the amount of water remaining in wet pulp sample after centrifuging. It is the ratio of water to dry fibre weight. WRV is useful as an indication of how tightly the fibre structure holds free water. WRV provides the better information about the refining or beating response of fibres and the water removal at press section. Beating is the most important physical treatment carried out on pulp before papermaking; it highly affects the physical properties of the prepared paper sheets. It serves the purpose of increasing the area of contact between the fibres by increasing their surface through fibrilation and by making them more flexible. As the beating revolutions increases the cutting and fibrillation of fibres takes place which leads to the formation of fines. The properties of fines differ greatly from the fibre fractions. The common definition of fines is the fraction that passes through a 200 mesh screen. Fines consist of cellulose, hemicelluloses, lignin and extractives. In chemical pulp the hemicelluloses content of fines is higher than in the fibre fraction. For mechanical pulps the lignin content of fines is higher than in the fibre fractions [15]. The increase in beating may affect the strength properties of paper.

The properties of paper are highly dependent on the properties of the pulp fibres. In addition to the specific surface area, the bonding ability of single fibres is highly relevant to the physical strength of the paper produced. Previous study suggests that Fibre–Fibre bonding strength is affected by the electrokinetic properties of the fibres, especially those related to

surface charge [1]. The fibre hydrophilicity and swelling, which are highly relevant to Fibre–Fibre bonding, are also affected by fibre charge [19].

1.2 Objectives

The objectives of this study have been planned stepwise as follows:

1. To carry out experiments on bleached hardwood, softwood, bamboo, wheat straw and bagasse pulp of known quality at different extent of refining by changing PFI Revolutions in laboratory PFI mill.
2. To examine the influence of refining parameters on Canadian standard freeness of stock, specific surface area, and specific volume of fibres.
3. To conduct experiments to evaluate fibre surface charge with Particle Charge Detector.
4. To evaluate the total charge by conductometric titration.
5. To carry out the experiments to evaluate water retention value (WRV) by centrifuge method.
6. To Study on the Beating of different raw materials at different revolutions through classification of fibres on Bauer McNett classifier.
7. To compare the parametric relationship among all the variables through graphs and develop univariate regression models through statistical methods.
8. To examine the effect of surface charge along with CSF values on strength properties of hand sheet of paper made in the laboratory.
9. To compare the Residuals and model predicted values among all variables through graphs and develop correlation coefficient through statistical methods.
10. To compare the parametric relationship between regression coefficient (R^2) and coefficient of determination (r^2).

1.3 Dissertation structure

Chapter 1 of this dissertation briefly introduces the study and its objectives. Chapter 2 summarizes the basic knowledge and literature information related to this area of research. The experimental methods are described in Chapter 3. Chapter 4 details the results of the influence of beating parameters on the carboxyl group content of various wood and non wood pulps. Lastly, Chapter 5 outlines the overall conclusions drawn from this Dissertation work.

CHAPTER 2 BACKGROUND LITERATURE

2.1 Effect of Beating/Refining on fibre Charge of Pulps

The strength properties of a sheet of paper depend on original qualities and strength of the fibres and to the extent of bonding between the fibres that make up the sheet. A paper sheet made from virgin pulp without beating/refining is characterized by low strength, bulkiness and rough surface. These undesirable characteristics can be changed to a large extent by treating the pulp mechanically. This mechanical treatment of fibres in water is termed beating/refining. This can be defined as the repeated passage of pulp through zones of compression and shearing. Beating or refining of pulp is an essential process of paper manufacture and is carried out to a greater or lesser degree in all paper and board mills.

The refining of any fibrous raw material is a complex process and the most influential of all of the papermaking processes. Mechanical treatment of chemical pulps has been reviewed [35]. Many structural changes to the fibres are attributed to beating, increased fibreswelling, fibre shortening, internal & external fibrillation, etc. [14, 24]. Apart from improving fibre properties, it has the greatest influence on product quality. Refining of pulp significantly contributes to papermaking process by affecting not only the quality of end product but also the runnability of the stock. A correct approach towards refining treatment is very essential for product with desired properties. The old adage that 'Paper is made in the beater (now refiner)' holds true for every paper product. The effects of refining are most often evaluated by freeness tests. This practice is somewhat an indirect way of measuring the effects of refining, since the reduction in drainage of the pulp, as measured by freeness, is not desirable in paper making process where high drainage is preferable. The three main actions of beating/refining are: internal fibrillation caused by the breakdown of fibre walls into separate lamellas which increases the flexibility of fibres so that during sheet formation the fibres conform to and around one another producing large areas of intimate contact; External fibrillation described as the creation and/or exposure of fibrils on the surface of the fibres; and generation of fines from fibres when these are no longer able to sustain compressive and/or shear forces during the treatment.

The sub-division of fibres into fibrils and the consequent holding of water in finer and more numerous capillary passages bring about a change in fibres that makes them more reluctant to allow the drainage of water from or through them. The fines in furnish, often produced during the refining process, tend to dominate the observed changes in freeness, as pulp is refined.

Because of increased surface and flexibility of pulp fibre in this condition, a greater degree of bonding takes place when the sheet is dried. Kraft fibres in particular are known to become more water-swollen during beating/refining, and there is often a high correlation between water retention value and inter-fibre bond strength. Refining develops various fibre properties in different ways and the purpose is to achieve maximum desirable effects with minimum undesirable effects [14].

In papermaking, beating to improve bonding and develop optimum strength properties deliberately enlarges the fibre surfaces. As fibre surfaces are peeled off during beating/refining, increasing amounts of charged fines are also formed. The primary fines consisting of parenchyma cells tend to contribute bulk and some opacity to a sheet of paper whereas the secondary fines produced by delaminating the outer layers of fibre during beating/refining tend to be slender and flexible ideal for bonding. Theoretically, as the surface is enlarged, the chemical components become more easily accessible and lignin and hemicelluloses are redistributed between pulp and water under the beating/refining action. It is well known that fibre fines tend to have more surface area per unit mass, compared to the fibres. If increased surface area due to mechanical action leads to more adsorption capacity in direct proportion to the increase in surface area, then as beating opens up the fibre surface, the fibre surface charge should increase with increased beating. This fibre surface charge is also shown to greatly influence the fibre swelling and paper strength properties [19, 20].

The effects of refining on the electrophoretic mobility distribution of spruce Kraft fibre fines have been determined [11]. It was found that increasing the level of refining did not appreciably affect the weak acid content or the average electrophoretic mobility over the range studied in this work. However, the cationic demand of pulp as determined using electrophoretic mobility has been reported to be increasing with increased degree of beating for bleached sulfite pulp [30] and softwood bleached Kraft pulp [5]. Herrington did not observe any change in total charge, as measured by potentiometric titrations, of various bleached eucalyptus sulphate wood pulps from dried sheets after varying degrees of refinement and presented that refining the pulp does not alter the specific surface charge in spite of the change in surface area. Changing the morphology of the pulp surface by beating has no effect on the charge per gramme of pulp [13]. He also presented that the specific surface charge for fines of softwood pulp is not very different from that of the unbeaten pulp. Gill [36] also studied the effect of refining on surface charge of bleached hardwood and softwood Kraft pulps. Polyelectrolyte titration was used as a measure of surface charge and the lack of correlation of surface charge with the degree of refining could not be explained.

Carrasco reported increase of total cationic demand of industrial bleached hardwood Kraft pulp using cationic polymer methyl glycochitosan (colloidal titration technique) with increased degree of beating. Further it was suggested that the fixation on cellulosic fibres is attained through 2 mechanisms: ionic exchange and adsorption by hydrogen bonds and Van der Waals forces [4].

It is evident that the effect of beating on pulp charge is more complex than the effect of chemical composition of pulp as both chemical and mechanical factors are involved. More studies are needed to understand the effect of beating on pulp charge. The individual contribution of fibres & fines to charge of pulp needs to be assessed and the better control of surface charge during beating of pulp may result in improved fibre-fibre bonding. So, better understanding of the mechanism of charge development is desired.

2.2 The role of charge on papermaking fibres

The significance of carboxylic groups or surface charge for the physical properties of mechanical pulp fibres has been presented earlier [1, 7 and 34]. The increase in strength is coupled both to the swelling of the pulp and to an increased concentration of carboxylic groups on the fibre surfaces. The water retention value increased with increasing pH and increasing carboxylic acid content. The increased swelling means that the flexibility of the fibres is improved which facilitates the formation of intra fibre and inter fibre bonds [7]. Ionization of the acidic groups results in increased swelling of the fibres due partly to the electrostatic repulsion between the negatively charged carboxylate anions [26, 27]. Pulp and paper properties are known to be related to swelling of cellulosic fibres. There is a linear correlation between the tensile strength of chemical pulp fibres and the degree of swelling of the fibres in different ionic forms [26]. The basic factors controlling swelling have been reported to be the type of cation bound to the acidic groups, the degree of dissociation and the ionic strength of the solution surrounding the fibre [20]. The concentration of the acidic groups on the surface of the fibres seems to have a relatively greater effect on tensile strength of paper than the total concentration of acidic groups [1]. Ampulski used a chemi-thermo mechanical pulp and presented that tensile strength is linked to both surface charge and bulk charge and can be described by the following mathematical model:

Tensile Strength = A (σ) + B (ρ) + C

Where σ = Surface charge density,

ρ = bulk (total – surface) charge density,

C = constant.

Though fair correlations were obtained with tensile & total charge and tensile & surface charge, the effect of high consistency bleaching (30%) appeared to be one of concentrating acid function on the surface of fibre and best correlation was obtained by combining the effect of surface charge with bulk charge [Breaking length (m) = 103 (σ) + 15 (ρ) + 54] [1]. This study also indicates that fibre surface charges can serve as one of the basic chemical parameters to characterise fibre surface properties, and that both surface charged groups and total charged groups are important for physical properties of the pulps [34].

A tentative explanation given is that the swelling of fibres increases with the amount of charge. Fibre flexibility increases with increased swelling. An increase in fibre flexibility promotes fibre conformability. Greater fibre conformability allows the fibres to get closer to each other and form more Fibre-Fibre contacts and form bonds. As a result the contact area and thus, the bonding area between the fibres increase [19]. Laine also reported that in terms of pulp and paper properties, the charge on fibre is of great importance for bleached hardwood than for bleached softwood Kraft pulp. Higher swelling for hardwood than softwood was reported because the charge on hardwood was higher because of higher xylan content of hardwood pulps, but also because the cell walls were thinner and contained more hemicelluloses, i.e. their elastic response to swelling was weaker. Fibre swelling and flexibility are affected by charge. In practice, there is opportunities especially in bleaching or other pulp treatments for enhancing fibre surface carboxyl group concentration and these may have practical value. The conditions at wet end also affect the total charge of the system. The surface carboxyl groups improve boding whereas carboxyl groups in fibre wall are responsible for fibre swelling and fibre wall flexibility. It would be worthwhile to see how surface charge and total charge are related to tensile strength and can be used to predict the tensile strength.

2.3 Effect of fibres on refining

A. Fibre delamination

Forces on the fibre in the refiner cause fibrils to move relative to each other, breaking internal bonds and thus causing fibre delamination. This has been clearly observed with the scanning electron microscope. Fibre delamination contributes to other changes in the fibre such as swelling and increased flexibility.

B. Fibre Swelling

Delamination of the fibres allows the entry of water into the fibre walls, causing the fibres to swell. This water breaks additional hydrogen bonds creating further swelling. Water

Retention Value has been shown to increase with refining, proving that there is an increasing amount of water bound to the fibre as the level of refining increases.

C. Increased fibre flexibility

Breaking of internal bonds allows fibrils to move relative to each other, making the fibres less resistant to deformation i.e. more flexible. This increased flexibility enables surface tension forces to bring more fibres into close proximity during consolidation of the web. This, in turn, increases the level of fibre/fibre bonding and thus influences paper strength, optical properties and other paper characteristics.

D. Removal of outer layers

The thin primary wall (or what remains of it following pulping and bleaching) and part of the S1layer can be removed by refining, exposing a new surface and allowing an increase in fibre swelling. The removed layers increase the fines level in the pulp and thus affect paper properties.

E. Micro creping of fibres and the introduction of other defects

These both affect the mechanical properties of the fibres. Micro creping produces a more extensible fibre and defects such as kinks and local ballooning of the Fibre can cause a reduction in the local fibre strength.

F. Curling and twisting of fibres

Fibre twisting and curling influence the network structure of paper and thus affect its properties.

G. Increased specific surface

The production of fine material with the removal of outer layers increases the specific surface. This is further increased by fibrillation i.e. loosening of the surface fibrils.

H. Fibre length reduction

This occurs with harsher beating. It has been used to reduce the flocculating tendencies of long fibre pulp but at the expense of tearing strength.

General effects on sheet properties on refining [29]:

- Drainage resistance (water removal resistance) increases.
- Tensile strength, tensile stiffness, burst strength, internal bonding strength, and fracture toughness increases.
- Tear strength of softwood fibres might slightly improve at first, but then decreases, whereas that of hardwood fibres at first significantly increases but then decreases after prolonged refining.
- Air permeability, bulk, absorbency, opacity and light scattering decreases.

- Brightness slightly decreases
- Fibre strength is little affected in refining.

2.4 Eucalyptus pulp and fibre quality requirements for the production of paper

Paper mills have targets for productivity, costs and efficiency. Eucalyptus pulp is a raw material for the manufacture of several grades of papers. For each paper grade and for each paper mill design, different may become the pulp quality requirements. This means that there is not a universal pulp, a pulp that may perform well everywhere.

Some of these properties are result of the wood quality, other depends on the conversion of wood to pulp (chipping, cooking, bleaching, pumping, blending, etc), and many are a combination of these two factors influencing the pulp quality. For example, some properties that are related to pulping and bleaching are: viscosity and degradation of cellulose chains, fibre deformations and individual fibre strengths, surface charges in fibres, etc. One important pulp property that is related to wood quality and pulp conversion is the hemicelluloses content in the pulp. This content depends on how high is the content in the wood and in the ability of the pulping process to preserve them in the fibres. There are other properties that are 100% dependent on the wood supply, the pulping and papermaking processes cannot modify them: fibre length, fibre wall thickness, vessel dimensions, etc.

A. The most important eucalyptus pulp and fibre properties

Today, the pulp and paper laboratories are squeezed by thousands of different types of analyses. Some mills are spending so much time on measuring everything, that the speed to take decisions and actions is completely affected.

The following pulp qualities parameters are key drivers to distinguish the different eucalyptus fibrous raw materials and to allow pulp furnish optimizations:

- Fibre population or the number of fibre per gram of pulp (associated to fibre coarseness)
- Individual fibre strength
- Fibre collapsibility
- Fibre bonding ability
- Fibre swelling and hydration
- Fibre deformations
- Fines content in the pulp

B. The most usual eucalyptus paper products

Eucalyptus pulps are special products to the manufacture of bulky and/or opaque papers. Today, Eucalyptus pulps are preferred raw materials in the manufacture of tissue, printing and writing, carton boards, industrial filter, base-paper for impregnation or coating, cigarette and many other papers. Eucalyptus fibres may be the sole fibre in the pulp furnish or to be part of a blend with other short and/or long fibres [10].

2.5 Softwood pulp uses in papermaking

Bleached softwood Kraft pulp is a heterogeneous raw material. The morphology of wood affects the length and cell wall thickness (CWT) distribution of fibres. Tracheid growth during spring and summer is very different. As a result, the CWT of latewood fibres is greater than that of early wood fibres, which makes latewood fibres less flexible. The tracheids of latewood are also often longer [17]. The differences in fibre dimensions are frequently in contradiction with the demands set for the fibres by different paper or paperboard grades. Improved strength may be a desirable property, while at the same time a smooth paper surface may be required. Long and stiff fibres improve the bulk of paper but impair its strength, and may have a negative effect on smoothness or other surface properties. Clearly, there is a need to control fibre properties better in papermaking to meet increased quality requirements.

The role of fibre flocculation in refining was identified long ago by [24]. An increase in the level of inter fibre contact increases the formation of coherent flocs which resist rupture in the flow, which changes the degree of non-uniformity in the suspension. At the contact points, several types of cohesive forces exist and the fibre properties may differ. For example, fibre length, fibre stiffness and fibrillation affect the magnitude of mechanical surface linkage and elastic fibre bending [18]. Different gap widths for the short and the long fibre pulps have been reported by [33].

2.6 Role of Wheat straw pulp

Non wood fibres have a long history as a raw material for papermaking. The use of this raw material declined in Europe and North America during the first half of this century as the amount of inexpensive and readily available wood fibre increased. Currently China produces about one-half of the world's non wood pulp while Europe and North America are relatively small contributors [9]. These two regions consume about 60% of the world pulp and paper production. Only four modern straw/grass fibre production sites exist in Europe and none in the United States. In some situations however, non wood plants may prove a viable fibre source in these industrialized regions.

Table 1 lists some of the reported wheat cell dimensions. Clearly, wide ranges of properties occur in the published literature. Some may be real, but some may depend on measurement technique. For example the difference in fibre length between [3] is extreme. A possible explanation for the difference in values could be that Cheng counted all of the cells while the other authors only included the fibres in their measurements.

***Table 1** Morphology of Wheat Straw*

	Avg Length (mm	**Avg. Diam. (□m)**	**NAFL (mm)**	**WAFL (mm)**	**MWAFL (mm)**
Atchison & McGovern [1987]	1.5	15	-	-	-
Cheng *et al.* [1994]	-	-	0.26	0.63	1.09
Hua & Xi [1988]	-	12.9	1.32	1.49	
Mohan, *et al.* [1988] (incl. min. - max.)	1.5 0.7 - 3.1	13.3 6.8 - 24.0	-	-	-
Utne and Hegbom [1992]	1.3	13	-	-	-

NAFL -- Numerical Average fibre Length; WAFL -- Weighted Average fibre Length; MWAFL -- Mass Weighted Average fibre Length

Since comparing reported values is difficult, several studies have specifically looked at the effects of growing conditions on fibre morphology.

Many of the literature reports are limited to the description of whole plant morphology and chemical differences. In addition, leaf, node and stem fractions may have different composition. The plant parts contribute significantly different mass as shown in Table 2.

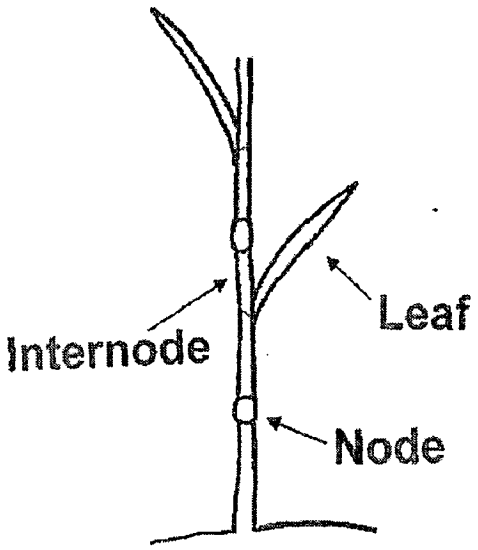

Fig. 1 Sketch of Wheat Straw

Table 2 Physical Content of Wheat straw

	Mass Percent*
Internodes	68.5
Leaves--Sheaths	20.3
Leaves--Blades	5.5
Nodes and Fines	4.2
Grain and Debris	1.5

*Ernst et al., 1960

Since the distinct sections of the plant have different functions, each section may also have different cells and chemical compositions. Table 3 summarizes the results of [2, 34]. When examining European wheat straw, Billa and Monties found the acid insoluble lignin (Klason lignin) content of the internodes to be higher than the leaves and nodes. Klason lignin is only part of the total lignin content with soluble lignin being the other part. Billa and Monties did not report the soluble lignin content of the different fractions.

Table 3 Chemical Composition within Wheat Straw

	Internodes	**Nodes**	**Leaves**
Klason Lignin (%)1	18.9±0.1	14.8±0.2	13.5±0.2
Total Lignin (%) 2		23.22	17.48
Holocellulose (%) 2	71.24		56.9
Ash (%) 2	5.93		12.06
Fibre Length (mm) 2	1.73	0.82	

1. Billa and Monties, 1995
2. Zhang, et al., 1990

With Chinese wheat straw, Zhang and co-workers found the stem section to have higher fibre lengths than the nodes, higher holocellulose, and less ash than the leaves. These trends suggest improved raw material qualities for the internodes, thus a potential for upgrading the raw material by fractionating out wheat straw components with less desirable properties.

2.7 Bagasse pulp uses in papermaking

Generally, non wood plant fibre pulps can be grouped into two broad categories:

- Common non woods or hardwood substitutes such as sugarcane bagasse, cereal straws, bamboo (shorter fibre species), reeds and grasses, esparto, kenaf (whole stalk or core Fibre), corn stalks, sorghum stalks etc.
- Specialty non woods or softwood substitutes such as cotton staple and linters; flax, hemp and kenaf bast fibres; sisal; abaca; bamboo (longer fibre species); hesperaloe etc.

Of the common non wood fibres, bagasse pulp mills are typically among the largest non wood mills which have been built because large volumes of bagasse are available in one spot

- the sugar mill. Typically, bagasse pulp is produced in integrated pulp and paper mills, and softwood Kraft or sulphite pulp is added to provide the strength requirements to the paper. However, specialty non wood pulp may be used instead of softwood Kraft or sulfite pulp thus producing a 100% non wood paper. The possible combinations are endless and can be adjusted to meet market requirements.

Furthermore, it is possible to add small quantities (up to 20 - 30%) of bagasse pulp to primarily wood pulp-based papers without impairing paper properties or paper machine runnability. This provides wood-based mills which are hardwood deficient but located within a region with available bagasse resources with the option of adding-on a straw pulping line to supplement their fibre requirements.

Agricultural residues such as wheat straws, bagasse, jute caddy, cotton stalk and other non woods like reed, sarkanda have proved to be economically viable sources of fibre supply. Non woods constitute 5-7% of the world wide fibre supply for production of paper. Environmentalist strongly supports the use of non woods along with agro-residues as a way to preserve natural forests.

Wheat and rice straw and bagasse are the potential agro-residues used for papermaking. Among these wheat straw and bagasse have well established themselves as a potential fibre sources and are commercially used for papermaking in many countries like India and China [25].

CHAPTER 3 EXPERIMENTAL MATERIALS AND METHODS

3.1 Experimental Design

In order to fulfil the objectives the experimental plan has been executed step by step as follows:

The experimental design is shown in fig.2. Different beaten pulps are used for the experiments. These beaten pulps are used for further tests.

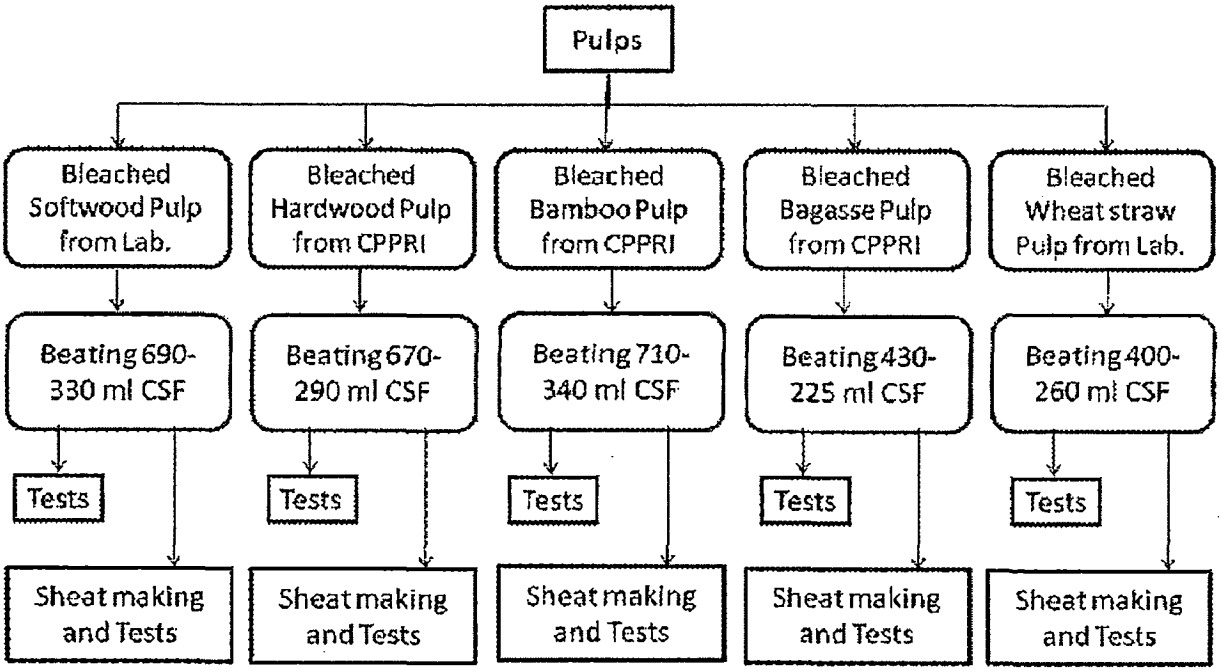

Fig. 2 The experimental procedures for different pulps at various stages.

3.2 Pulp characteristics

For the purpose five different pulps namely Bleached Softwood Pulp, Bleached Hardwood Pulp, Bleached Bamboo Pulp, Bleached Bagasse Pulp and Bleached Wheat straw Pulp were selected. Three different Pulps namely Bleached bagasse pulp, Bleached Bamboo Pulp and Bleached Hardwood Pulp were procured from "Central Pulp and Paper Research Institute (CPPRI)" Saharanpur. Two different Pulps namely Bleached Softwood Pulp and Bleached Wheat Straw Pulp were procured from laboratory.

All the pulps were tested for moisture Content and Percentage of Consistency. Moisture Content was measured by the TAPPI test method T 412 om -94. Bleached baggase pulp, Bleached Hardwood Pulp and Imported Softwood Pulp are already in air dried condition with dryness 25%, 33% and 25%. Bamboo pulp was bleached at Laboratory using a DEDD to a brightness of 88% and beaten at 10% consistency of pulps in a PFI beater. However, Wheat Straw pulp was bleached at Laboratory using a DEDD to a brightness of 80% and beaten at 10% consistency of pulps in a PFI beater.

3.2.1 Chemicals

The analytical grades of NaOH, HCl, and NaCl were used in the experiments. Polydiallyldimethylammonium chloride (Poly-DADMAC, molecular weight 150–200,000 g/mol) and sodium-polyethylene sulphate (PES-Na, molecular weight 19,100 g/mol) were reagent grades (ATA Scientific Pty. Ltd.). These chemicals were diluted with deionised water with a conductivity of 8×10^{-4} mS/cm to the desired concentration before use. Nitrogen was used to prevent the absorption of carbon dioxide into the test samples during the conductometric titrations.

3.3 PFI beating

Operation

The PFI Mill consists of an internal roll with beating bars revolving inside a heavy bowl (bedplate). Both the roll and bedplate rotate, but at different speeds. As the roll is pressed against the bedplate it transfers energy to the fibres.

Pulp consistency is constant throughout the operation as roll and bedplate revolve at constant speed (both in the same direction but at differing speeds). The rate of pulp development is governed by the pressure between the roll and bedplate which can be adjusted to suit the pulp type under evaluation. The degree of beating is proportional to the beating time. Separate pulp samples are required for each point on the beating development curve. At 10% consistency the pulps are subsequently refined in a PFI beater following (Fig.No.3) TAPPI Test Method T 200 sp-96.

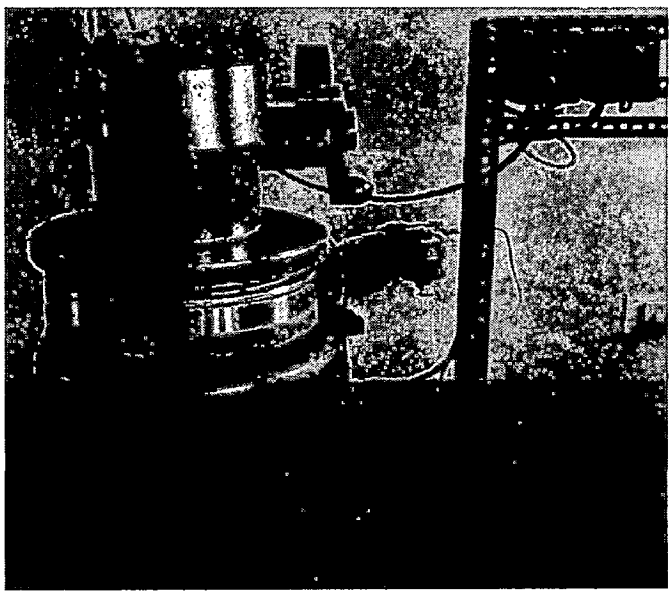

Fig. 3 PFI beater.

Specifications

Beating in the PFI Mill is carried out automatically once the pulp charge has been placed in the bowl. The beating elements consist of a stainless steel roll with 33 chiselled bars and a smooth sided circular bedplate. The bedplate is charged with pulp, forming an endless band around the circumference. The roll rotates with a higher peripheral speed than the bedplate, the roll bars cut out sections of the pulp band, transporting them into the beating zone. The beating pressure is obtained from a load applied by means of a weight lever action via a cantilever mounted on the base of the supporting pillar that is rigidly attached to the frame. Brass weights are attached to the lever arm to vary the load.

In the standard operating procedure the load is applied directly to the pulp and the beating gap between roll and bedplate forms naturally. The PFI Mill also allows pulp to be beaten with a fixed gap set by means of a micrometer placed against the pillar adjusting the amount of swing made by the cantilevered arm. This practice is used also for grinding-in and calibration purposes.

The rotating speed of the roll is set to 1440 ± 30 r.p.m. and the bedplate to 720 ± 20 r.p.m., under no-load conditions. The roll and bedplate are driven by separate motors and both rotate clockwise (this direction is reversed for grinding-in). The normal beating pressure with the fixed weight is 1.8 kgf/cm of bar height and with the additional weight 3.4 kgf/cm.

3.4 Canadian standard freeness

The apparatus (Fig. 4) consists of a drainage chamber and rate measuring funnel on a bench mounted support. The drainage chamber is fitted with a calibrated screen plate through which the water drains leaving a pad of pulp. The bottom is sealed with a quick release lid opened at the start of the test. The top is similarly sealed but the lid is fitted with a petcock, which is opened to release the vacuum created during drainage. The rate measuring funnel is a cylindrical top fitted over a conical lower section. At the base of the cone is a calibrated orifice which governs the rate of discharge from the cone. Excess water is led off through a side orifice, at a set critical distance above the orifice, into a measuring cylinder. The volume of water collected is the freeness value. Pulp freeness was tested using Canadian Standard Freeness tester according to (TAPPI, 1985).

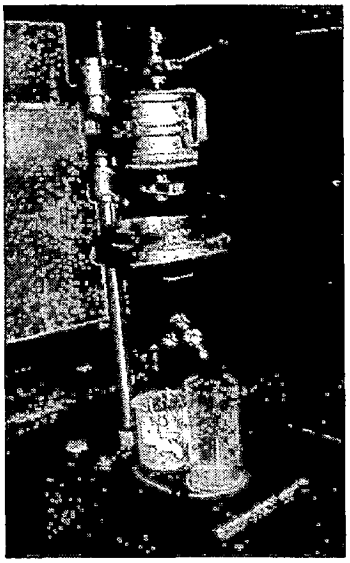

Fig. 4 CSF Tester.

3.5 Determination of charge

All pulps were washed according to the following procedure:

Before the charge measurements were undertaken, the pulp samples were converted fully protonated form by soaking the pulp at 1% consistency in 0.01 M hydrochloric acid for 16 h (final pH of 2.2). The pulp was then vacuum filtered using a Buchner funnel and washed several times with the deionised water until the pH of the water filtrate was close to 6.0. The carboxyl groups on the fibres were then converted to their Na form by a procedure developed by [32]. After each titration, the amount of fibres in each sample was determined gravimetrically by filtering the pulp on pre weighted filter paper and drying in an oven at 105°C until a constant weight was obtained [23].

3.5.1 Polyelectrolyte titration

The polyelectrolyte titrations are performed using a MUTEK Particle Charge Detector (PCD-02, Fig.No.5).The pulp sample (0.5 g) is diluted with 100 g of 0.001N poly-DADMAC and stirred by a magnetic stirrer for 2 h. During this time the cationic polyelectrolyte completely neutralized the anionic charge in the pulp. The solid content of the pulp is removed on a #100 mesh nylon sieve and 10 ml of the filtrate is pipette into the cell of PCD-02 (MUTEK) and titrated with 0.001 N PES-Na to the endpoint where the streaming potential reached 0 mV. The rate of titration is controlled at 0.1 ml/min. In addition, 10 ml of poly-DADMAC solution is titrated with PES-Na to the neutral point to determine the blank value [23].

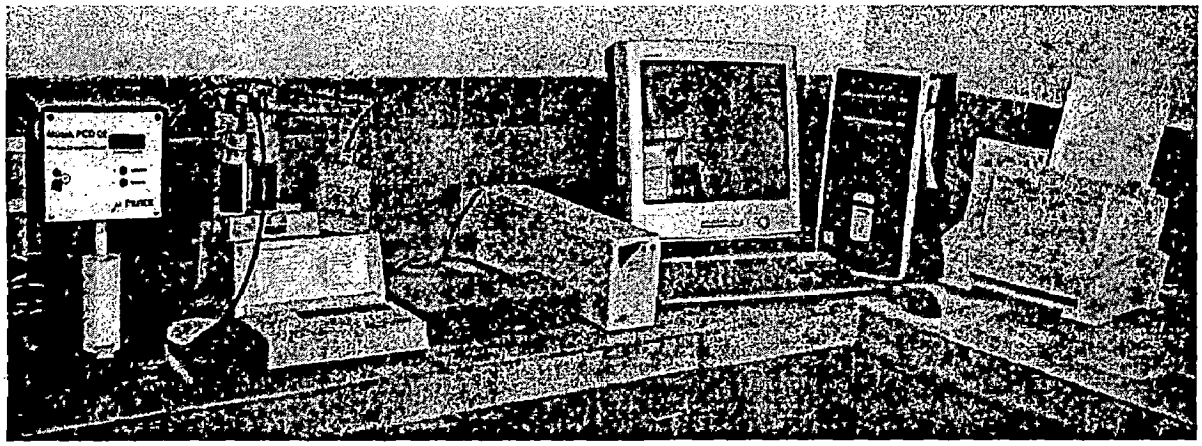

Fig. 5 Mutek Particle Charge Detector (PCD-02).

The specific charge density of the sample is calculated by the formula below:

$$q = \frac{(V_p - V_b) \times c \times 1000}{w}$$

Where

q is the specific charge density (mmol/kg),
V_p is the volume of titrant used for pulp (ml),
V_b is the volume of titrant used for blank (ml),
c is the concentration of titrant (mol/l), and
w is the solid content of pulp (g).

The following example is shown in the Appendix A.

3.5.2 Conductometric titration

Approximately 0.5 g of the protonated pulp was dispersed in 1 mM sodium chloride (100 ml) and an addition of 0.5 ml of 0.05 M HCl was made before the start of each titration. The titration was performed with 0.05 M NaOH at 25 °C using a 718 STAT Titrino Auto titrator from Metrohm and a LC-81 conductivity meter from TPS Pty. Ltd. The conductivity measurements were made every 30 s after each addition of 0.05 ml of alkali solution. The conductometric titration was based on changes in conductance of the suspension. The addition of HCl was made before the start of the titration. Initially the conductance decreased due to the neutralization of the added HCl. The additional alkali reacted with the weak acid groups bound to the fibres, causing a buffering effect stabilising the conductance. After the neutralisation of these weak acids, further addition of the alkali raised the conductance. The resultant conductance of the suspension was plotted against the volume of the alkali added. The fibre charge was then calculated using the volume of the alkali required to reach the second inflection point from the first inflection point of the plot [23].

The Total charge of the sample is calculated by the formula below:

$$\text{Total charge} = \frac{(V_2 - V_1) * c}{m}$$

Where

$V_2 - V_1$: Difference between the charges of the 0.1 M NaOH added, ml and the reacted 0.1 M NaOH added, ml indicates the charge amount neutralized in the sample.

c: Concentration of the titrant, i.e. here 0.1 M NaOH added, ml.

m: 0.5 g of the original sample are used for titration.

The following example is shown in the Appendix B.

3.6 Pulmac Permeability Test

The specific surface area and specific volume of the pulp are measured using Pulmac Permeability Tester (Fig. 6) as per the instructions mentioned in the manual of the instrument manufacturer as under:

3.6.1 Sample Preparation

a) Quantity of pulp required

About 8 grams of pulp are required for an accurate determination of the pulp's permeability characteristics in the Pulmac Permeability Tester. When working with slow draining pulps, such as well-refined chemical pulps or ground wood pulps, it may be advantageous to reduce the sample size in order to minimize the time required for forming the pad. It is not recommended that less than about 4 grams of pulp be used in the apparatus, since the effect of any non-uniformity in pad formation will be accentuated with thin pads.

b) Consistency to be used for pad formation

The consistency required in the formation tube in order to ensure a well-formed pad will vary with the type of pulp. It has been found that good reproducibility is obtained with ground-wood, which does not have a severe tendency to flocculate, at consistencies as high as 0.6%. Long Fibred pulps and finishes which do exhibit flocculating tendencies should be diluted to about 0.5%. Since consistency is not an important variable with the Pulmac Permeability Tester, rapid control of consistency during pad formation is not critical.

c) Sample Disintegration and Deaeration

The sample should be thoroughly disintegrated. The pulp slurry must be deaerated prior to pad formation. This is most readily accomplished by gently stirring the pulp slurry with a magnetic stirrer under vacuum for approximately 15 minutes.

d) Temperature

The slurry should be adjusted to be room temperature as this variable enters in to the calculation of specific surface and specific volume. Temperature is most easily controlled if

the temperature of the slurry and that of the water used in the Permeability Tester for the pressure drop-flow rate determinations are roughly equal at room temperature

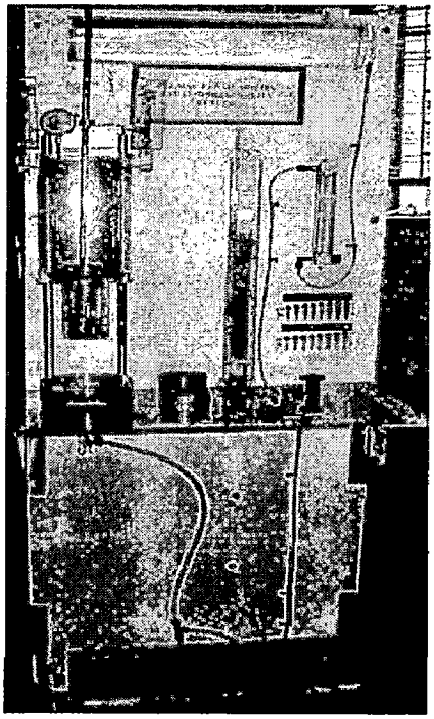

Fig. 6 Pulmac Permeability Tester

3.6.2 Operation of the Pulmac Permeability Tester

A. Check to see that no air is trapped under the septum or in any of the tubing of the apparatus as described in section I.

B. Close the overflow valve (L) of the formation tube, raise the piston (P), and secure with the thumb screw (S). Pour the deaerated slurry in to the formation tube in such a manner that there is a minimum entrainment of air.

C. Gently stir the slurry, and then allow the slurry to come to rest so that there are no larger circular motions in the filtration tube.

D. Open the drain valve (I) to allow the pad to form on the septum.

The drain valve can be used to control drainage rate. However, under most circumstances, it is found most suitable to have the valve fully open.

E. Gently stir the slurry in the upper portion of the formation tube to prevent flocculation. In no case should the stirring extend below the level of the conical section of the formation tube and no gross circular motion should be induced in the filtration tube.

F. Allow formation to continue until the level of the slurry in the tube is about 1/8 inch above the bottom of the cone. Wait a few minutes for the pulp slurry to settle, leaving a thin layer of water above the slurry.

G. Lower the piston to the surface of the water, and by gently twirling the piston force all air out from under the piston face.

H. Slowly lower the piston on to the mat. Allow the piston to descend below the overflow weir.

This procedure for forming the mat and placing the piston is designed to make it simple and certain that no air is entrapped under the face of the piston

I. Open the filtration tube overflow valve and leave open. Allow the excess water to drain through the waste drain line to the level established by the sharp-edged over-flow weir.

J. Place the 500 gram weight (T) on the piston collar to pre compact the bed. Select the spacer (U) which just fits under the collar with the 500 gram weight in order to ensure compaction of the bed to the precise thickness of the spacer.

K. Open the manometer valve (J) and rotameter valve (B), and establish a flow rate through the rotameter sufficient to give pressure drop of 1.5 cm. as indicated by the manometer.

By Pre Compacting the bed with a 500 gram load and limiting the pressure drop at the maximum bed thickness to about 1.5 cm, the compaction pressure exerted by the fluid drag forces within the bed will never be more than about 10% of the mechanical compaction exerted on the bed by the piston. It is important to keep the fluid drag forces to a fraction of the mechanical compaction forces in order to ensure a uniform density throughout the bed. The uniform bed density is required in order to calculate accurate values for the specific surface and specific volume of the pulp.

L. When the readings have stabilized, record the rotameter reading, the pressure drop indicated on the manometer, and the spacer length. Close the manometer valve and rotameter valve. Replace the existing spacer by the next shortest spacer, and continue until six to eight sets of data have been recorded. It may be necessary to add a second 3.0 kilogram weight to the piston in order to compress the bed to the thickness established by the shorter spacers.

M. Measure the temperature of the water by inserting a thermometer above the piston.

N. At the conclusion of the experiment, close all valves. Unclamp the filtration tube, raise and secure it in the raised position. The water above position will simply floe out the waste line and the sample will be retained between the piston (which is still weighted) and the septum.

O. Remove the weights from piston raise and secure it with thumb screw.

P. Remove the pad and dry at 105^0C for an accurate determination of the pad weight.

It is possible to estimate the pad weight by knowing the consistency and quantity of slurry used in the formation of the mat. Because of the many possible difficulties in determining

consistency accurately, and in maintaining a uniform dispersion of the pulp during the consistency and volumetric measurement, it is preferable to dry the bed after experiment for precision in the pad weight.

No air will normally be sucked under the septum during removal of pad. All that is required in order to prepare the Pulmac Permeability Tester for another sample is to lower and clamp the filtration tube and pour in another sample of deaerated pulp.

These data were then used to calculate the specific surface area and specific surface volume of the pulp using the fallowing equation (Robertson and Mason, 1949):

$$\left[\frac{c}{R_P}\right]^{1/3} = \left[\frac{1}{k\,S_W^2}\right]^{1/3} (1 - VC) \quad \ldots\ldots (1)$$

With $R_P = \frac{A^2 \Delta P}{q(W)\eta}$ ..... (2)

And $c = \frac{W}{AL}$ ..... (3)

Where

R_p – Specific resistance to permeation, cm/gm.

A - Pad area, cm^2

ΔP – Pressure drop, dynes/ cm^2

q- Flow rate, cm^3/sec.

W – Pad weight, gm.

η - Viscosity, poises (gm./cm/sec.).

L – Pad thickness, cm.

K – Kozeny constant.

S_W - Pulp specific surface, cm^2/gm.

v- Pulp specific volume, cm^3/gm.

c- Pad density, gm/cm^3.

Plotting equation (1) in the form $(c/R_P)^{1/3}$ versus c should yield a straight line with an intercept on the horizontal axis equal to 1/v. This relationship is indicated in the Fig.7.

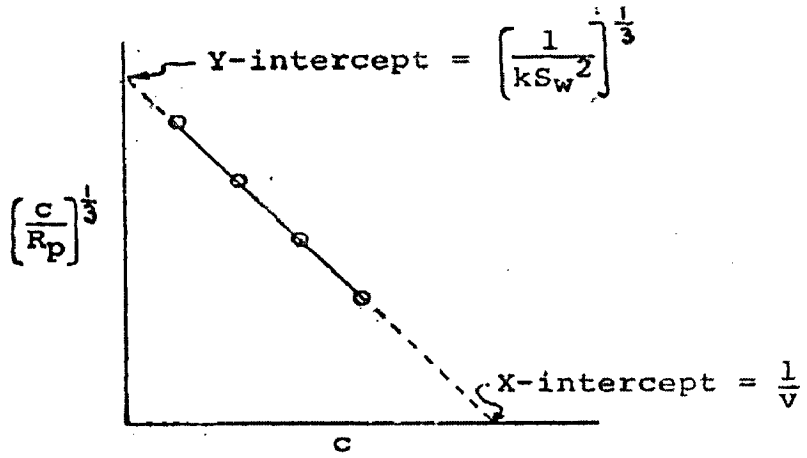

Fig. 7 Factor $(c/R_P)^{1/3}$ versus density(c).

The kozeny constant is usually taken to be 5.55 for pulp fibres.

The following examples are shown in Appendix C.

3.7 Water retention value (WRV)

Water retention value is a measure of the water retained by a wet pulp specimen after centrifuging under standard conditions.

The WRV of the pulp is measured through centrifuge method. The pulp sample 0.18 g O.D. basis is slurried with 18 ml water. The slurry is divided into four small cylinders having 60 mm mesh and weight of 38.785 gm. The four cylinders are gently placed in bowl of centrifuge. The operation starts and continues for 30 min. at 2400 Nos. Thereafter the pulp is weighed. The pulp then left for oven drying and again oven-dried weight is measured. The water retention value test was carried out by TAPPI 1991/15-56 Useful Methods. Using the fallowing formula the WRV of the pulp is measured.

$$\text{WRV} = \frac{\text{wet weight} - \text{Dry weight}}{\text{Wet weight}} \times 100$$

The following examples are shown in Appendix D.

3.8 Bauer McNett Classifier

Classification of fibre is carried out in Bauer McNett classifier (Fig. 8), the pulp fibres were allowed to pass through different screens having different mesh sizes as +16, +30, +50, +100, and +200 by maintaining water flow rate as 11.355 L/min. The process starts and continues for 20 min [31].

After 20 min operation, shut off the water and motor of stirrer. The drain plugs were removed and allow the contents to drain into the cups. The fibre is collected from the bottom of each container and kept into oven for further calculation. The classification of fibres is carried out by TAPPI testing method T 233 cm-82.

Fig. 8 Bauer McNett classifier

The amount of fibres which passes through 200 meshes are treated as fines and can be calculated as:

$W_6 = W - (W_1+W_2+W_3+W_4+W_5)$

W_1, W_2, W_3, W_4 and W_5: Weight of fibres collected over mesh +16, +30, +50, +100, and +200 respectively; W_6: amount of fines pass through +200 mesh screen.

3.9 Lab hand-sheet preparation

Pulp slurry equivalent to 1.2 g O.D solid is taken in British sheet former for the preparation of approximately 60 g/m^2 paper hand sheet. The hand sheets are pressed in hydraulic press at 10 kg/cm^2 pressures and then air- dried. After making sheets, they were allowed to dry in open atmosphere minimum for 24 hours. Finally hand sheets are tested for all properties as per standard. The process was carried out by TAPPI testing method T 205 om-88. For clarity the important tests are defined and the methods of determinations are described as under:

3.10 Hand sheet properties

3.10.1 Grammage

Grammage is a metric measure of paper weight in grams of one sheet of paper that is one square meter in area-not dependent on basic sheet size or paper grade. Paper of specific area (200 cm^2 circular disc) through standard cutter is measured and weighed in electronic monopan balance. The results is the converted to gm per metre squared. The following examples are shown in Appendix E.

Tensile Strength

Tensile strength is the maximum load applied in breaking a tensile test piece of specific dimension in tensile tester (Alwetron/ Instron etc.) divided by the original cross-sectional area of the test piece. It is now measured as kg/15mm.

Procedure of measuring tensile strength is as follows:

Each sample is cut into 15 mm wide strips and the two clamps that held the test specimen are initially set to a test span of 10 cm. The test specimen is stretched at a constant speed of 25 mm/min until it failed then determine the tensile strength. Breaking length and tensile index are estimated as per standard.

$$\text{Breaking length} = \frac{\text{Tensile strength}}{\text{gsm}}$$

$$\text{Tensile index} = \frac{\text{Tensile strength (N/m)}}{\text{gsm}}$$

3.10.2 Tear Strength

Tear strength is the maximum force required to tear a specimen in Elmendorf tear tester, the force acting substantially parallel to the major axes of the test specimen.

Tear Strength = F / t

Where:

F = force, N (kg, lbf).

t = specimen thickness, m (cm, inch).

Procedure of measuring tear resistance is as follows:

Clamp the sheets so that their glazed sides face the axis of the instrument and the greater part of the specimen is held in the fixed, not the moving jaw. Then determine the tearing strength and tear index as per standard formula.

3.10.3 Burst strength

Burst strength is the pressure required breaking a fabric by expanding a flexible diaphragm or pushing a smooth spherical surface against a securely held circular area of fabric. It is measured as Kg_f/cm^2.

Procedure of measuring bursting strength is as follows:

All samples are tested for compression testing machine. Place the sample in the ring clamp as flat as possible with no wrinkles or tension and tighten the clamp. Centre the ball on the sample and set the assembly in the CBR machine. Operate the machine at top speed but no more than 300 mm/min until the fabric is ruptured by the steel ball read and record the

bursting pressure of the fabric from the CBR machine dial. Calculation of burst factor or burst index is made based on usual standard procedure.

3.10.4 Folding endurance

Folding endurance is the paper test that measures the number of double (back and forth) folds that can be made on a sheet of paper, under tension, before it breaks.

Procedure of measuring double folds is as follows:

10 mm portion of the strip needs to be clamped in the lower (moving) jaw and the exact tension of 1 kg applied, leaving the extra length of the strip projecting through the upper jaw. Because the part of the strip above the upper clamp is not appreciably affected by the test, the upper end of the strip can be used for another fold test making the fold in the part of the strip that is above the clamp.

The standards of measurement and procedure followed are depicted in Table-4.

Table 4 *The following standards are used to test the properties of hand sheets*

Properties	Standards
GSM	T 410 OM-02
Tensile strength	T 456 OM-03
Tear strength	T 414 OM-98
Bursting strength	T 403 OM-02
Folding endurance	T 511 OM-02

The calculation procedures are exemplified as sample calculation, are shown in Appendix E.

CHAPTER 4 RESULTS AND DISCUSSION

As indicated in Chapter 4 each refined pulp sample was analysed to obtain freeness, surface charge, specific surface area and specific volume. The conductometric titration is used to measure the total charge of pulp whereas the polyelectrolyte titration is used to measure the surface charge of pulp as accessible to Poly-DADMAC. Comparison of different CSF and ^{o}SR values are shown in Table 5 whereas in Table 6, the values of surface charge, and total charge are compared as a function of CSF are depicted .The calculated values of charge ratio are also shown therein. Table 7 depicts average specific surface area and specific volumes are compared as a function of freeness. Comparison of water retention value at various revolutions and freeness levels are shown in Table 8. Table 9 shows the comparison of fibre fractionations for various pulps. In Table 10 the strength properties (tensile index, tear index, burst index and double fold values) of the handmade sheet made from British sheet former are compared as a function of CSF with PFI revolutions as parameter. Calculations procedures are shown in Appendix A to E along with the values of conductivity and permeation resistance. In all cases freeness values and PFI revolutions are used as independent parameters. The regression coefficients of different parameters as functions are shown in Table-11.

From the plethora of data, various figures are also drawn to show the parametric effect on the properties of paper with surface charge and total charge as the major parameters. These are discussed in the following paragraphs.

4.1 Relationship between freeness and PFI revolutions

The values of CSF are shown in Table 5. In Fig. 9 pulp freeness is represented as a function of PFI revolutions. Fig. 10 depicts ^{0}SR is represented as a function of PFI revolutions It was apparent that the pulp freeness decreased more markedly for eucalyptus pulp than softwood pulp. Similar pulp freeness values for the five pulps were achieved by using different ranges of PFI revolutions. The required PFI revolutions for refining to freeness were highest for softwood pulp followed by eucalyptus pulps in a decreasing order.

***Table 5** Different freeness level at various PFI revolutions*

Pulp	PFI Revolutions, Nos.	Freeness, ml CSF	^{0}SR
Hard wood pulp (Eucalyptus)	0	670	14.03
	1000	540	22.34
	2000	460	28.08
	3000	370	35.34
	4000	290	42.88

Softwood pulp	0	690	12.83
	2000	610	17.73
	3000	500	25.14
	4000	460	28.08
	5000	330	38.95
Bamboo pulp	0	710	11.66
	2000	560	20.99
	4000	440	29.61
	5000	340	38.02
Wheat straw pulp	0	400	32.8
	500	320	39.9
	1000	260	46.1
Bagasse pulp	0	430	30.39
	1000	390	33.63
	1500	340	38.02
	2000	270	45
	2500	225	50.25

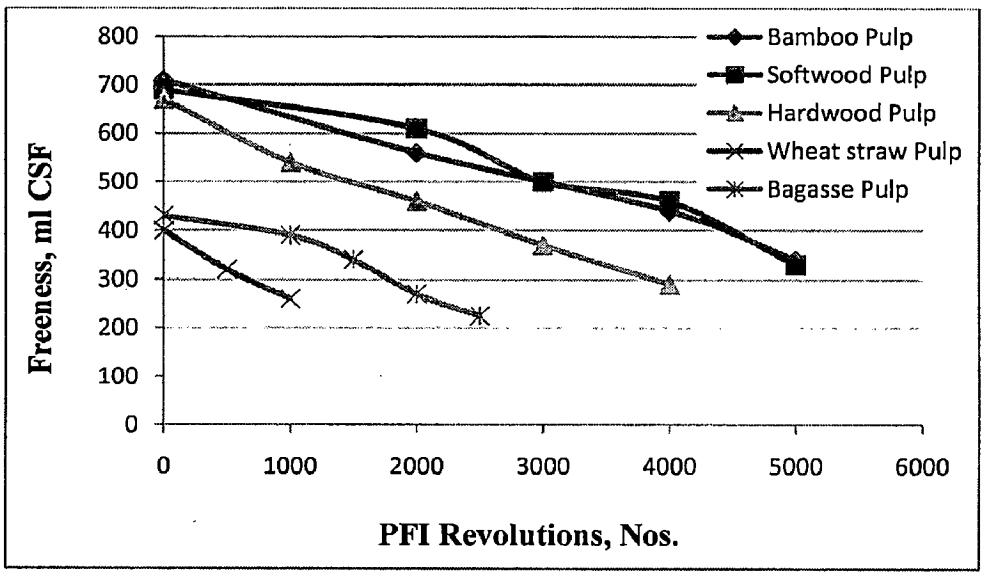

Fig. 9 Effect of refining on pulp freeness of various wood and non wood pulps.

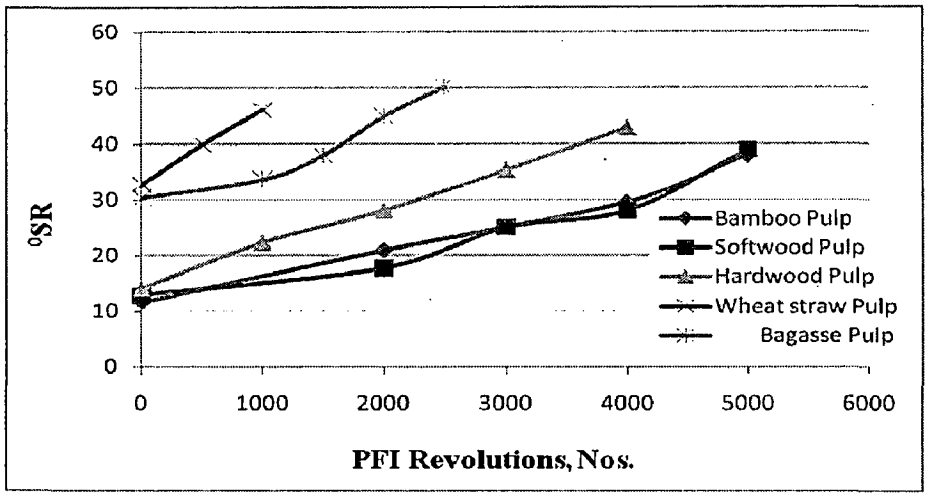

Fig. 10 Effect of refining on Schopper Reigler (°SR) of various wood and non wood pulps.

4.2. The effect of refining on fibre surface charge and total charge of pulp

The values of fibre surface charge of refined pulps as shown in Table 6 are plotted in Fig. 11.

***Table 6** the surface charge, total charge and charge ratio of different nonwood pulps and wood pulps.*

Pulp	PFI Revolutions, Nos.	Freeness, ml CSF	Surface charge, µeq/g	Total charge, µeq/g	Charge ratio (Surface/Total)%
Hard wood (Eucalyptus)	0	670	14.01	73.25	0.19
	1000	540	15.94	76.34	0.20
	2000	460	18.11	74.12	0.24
	3000	370	20.43	77.82	0.26
	4000	290	23.35	75.65	0.30
Softwood	0	690	11.05	69.8	0.15
	2000	610	11.98	67.91	0.17
	3000	500	13.13	66.89	0.19
	4000	460	14.73	66.83	0.22
	5000	330	16.11	68.76	0.23
Bamboo	0	710	23.76	130.54	0.18
	2000	560	25.17	133.33	0.18
	4000	440	26.99	137.23	0.19
	5000	340	28.78	134.75	0.21
Wheat straw	0	400	34.56	151.95	0.22
	500	320	37.12	150.86	0.24
	1000	260	42.64	152.66	0.27
Bagasse	0	430	9.95	92.81	0.10
	1000	390	13.65	93.98	0.14
	1500	340	17.04	91.12	0.18
	2000	270	24.14	90.9	0.26
	2500	225	29.87	92.1	0.32

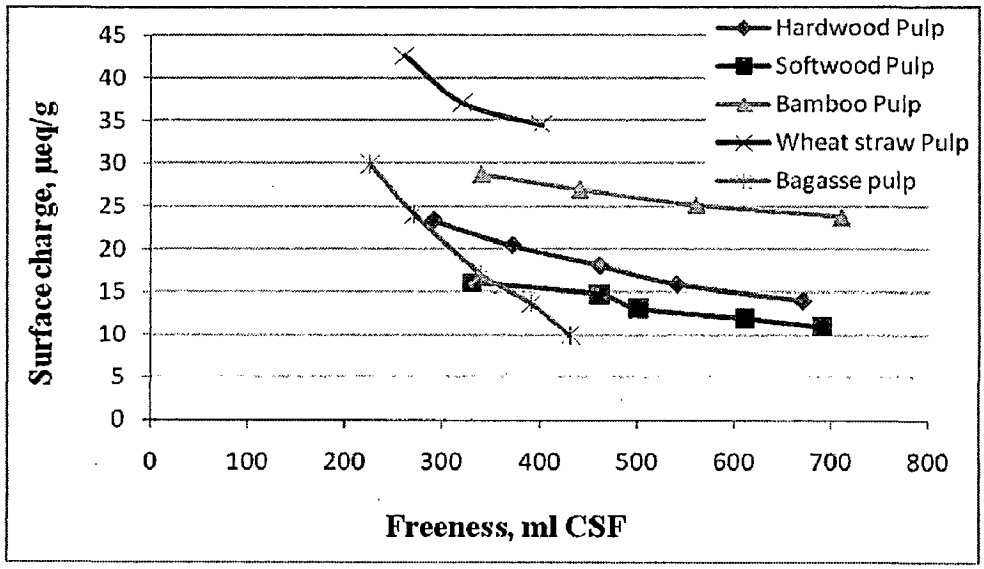

Fig. 11 Effect of refining on Surface charge of pulps at Freeness levels.

4.3 The effect of refining on specific surface area and specific volume

The specific surface area and specific volume are the pulp properties that influence the characteristics of paper product. The specific surface area characterizes the amount of surface area per unit weight that a wet pulp exhibits whereas the specific volume characterizes the swollen volume of the pulp on a unit weight basis. Table 7 depicts average surface area, and specific volume as a function of freeness. For all the beating pulps analysed, the specific surface area of pulps increased linearly with further refining treatment (decreased pulp freeness) of the same pulp, consistent to the fact that refining of pulp induced fibrillation of fibres and formation of fines. Both contributed to the increase of specific surface area. In fig. 12 and fig. 13, the specific surface area and specific volume is increased with decreasing the various freeness levels.

***Table** 7 Specific surface area and specific volume at various freeness levels*

Pulp	PFI Revolutions, Nos.	Freeness, ml CSF	Specific surface area, m^2/g	Specific volume, cm^3/g
Hard wood (Eucalyptus)	0	670	1.53	4.05
	1000	540	2.11	4.36
	2000	460	2.73	4.7
	3000	370	3.23	5.16
	4000	290	3.83	5.65
Softwood	0	690	0.71	4.01
	2000	610	0.74	4.27
	3000	500	0.78	4.45
	4000	460	0.83	4.77
	5000	330	0.87	5.14

Bamboo	0	710	1.48	3.26
	2000	560	1.63	4.87
	4000	440	2.41	5.07
	5000	340	2.98	6.26
Wheat straw	0	400	1.8	3.12
	500	320	1.83	3.96
	1000	260	1.87	4.62
Bagasse	0	430	2.09	3.21
	1000	390	2.69	3.5
	1500	340	2.84	3.84
	2000	270	3.44	4.69
	2500	225	3.5	4.75

It should be noted that severe refining can lead to fibre shortening, resulting in increased specific surface area of the pulps, and subsequently increased the fibre surface charge. For all the pulps, the surface charge is found to be approximately proportional to the specific surface area.

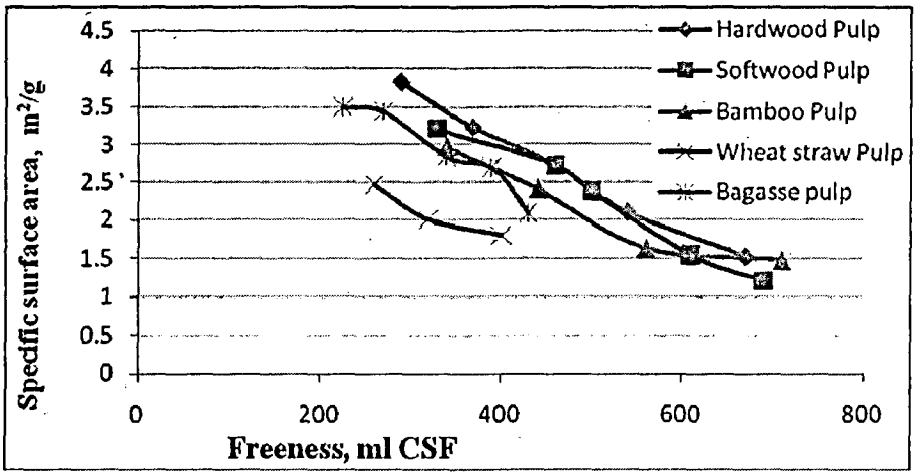

Fig. 12 Effect of refining on specific surface area at various freeness levels.

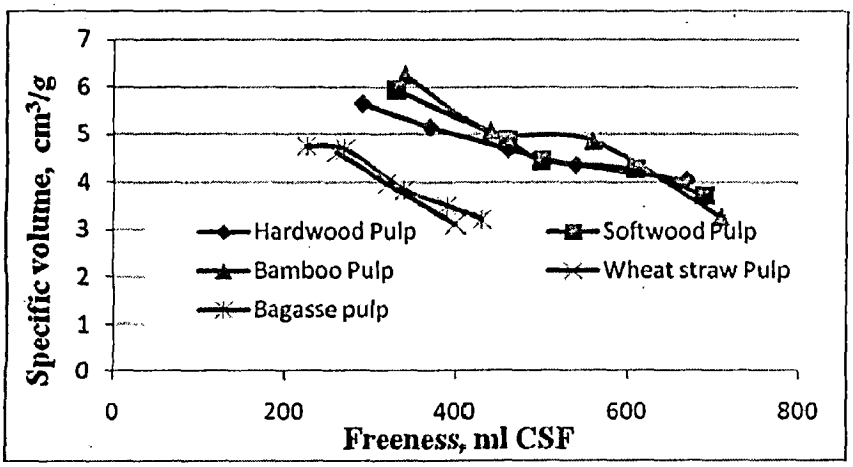

Fig. 13 Effect of refining on specific volume at various freeness levels.

4.4 The effect of refining on water retention value (WRV)

The water retention value at various freeness levels are shown in Table 8. The difference between water retention values of unbeaten samples and beating samples is high which shows that the fibrillation of fibres is more in this case.

Table 8 *Water retention value at various revolutions and freeness level*

Pulp	PFI Revolutions, Nos.	Freeness, ml CSF	Water retention value, %
Hard wood (Eucalyptus)	0	670	98
	1000	540	115
	2000	460	134
	3000	370	153
	4000	290	167
Softwood	0	690	113
	2000	610	196
	3000	500	230
	4000	460	275
	5000	330	292
Bamboo	0	710	113
	2000	560	163
	4000	440	238
	5000	340	292
Wheat straw	0	400	298
	500	320	393
	1000	260	404
Bagasse	0	430	176
	1000	390	204
	1500	340	232
	2000	270	256
	2500	225	278

The effect of refining on water retention values at different freeness levels is shown in fig. 14. WRV is increased with increasing the revolutions and also decreasing the freeness levels. WRV data is generally used in the measurement of water content as a percentage of oven dry weight. Results describe the higher initial beaten fibres has the higher water retention value. As fibres are beaten the cell walls are delaminated and the microspores are created. Result could indicate that the portion of internally laminated fibre cell wall exist much more in higher beaten fibres as water retention value is consistent increases with beating as shown in fig. 14. Also beating increases the pulp drainage resistance increased due to an increased in surface area (mainly fines formation). Internal fibrillation increases the fibre swelling and flexibility by loosening the cell wall structure and external fibrillation increases the outer

surface of fibres.WRV is depend on the surface charge. According to surface charge the WRV are increased is shown in fig. 15.

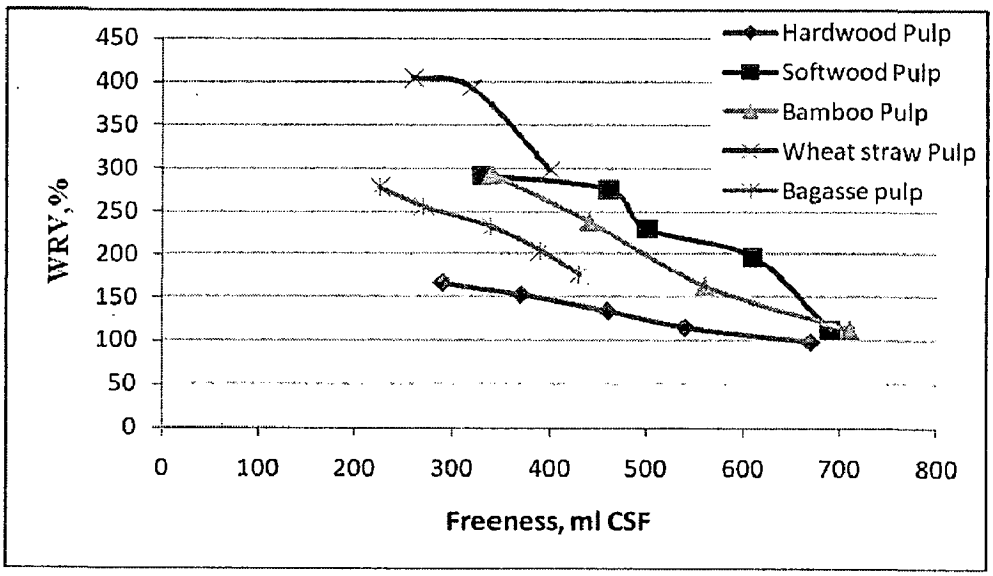

Fig. 14 Effect of refining on Water retention value (WRV) at various freeness levels.

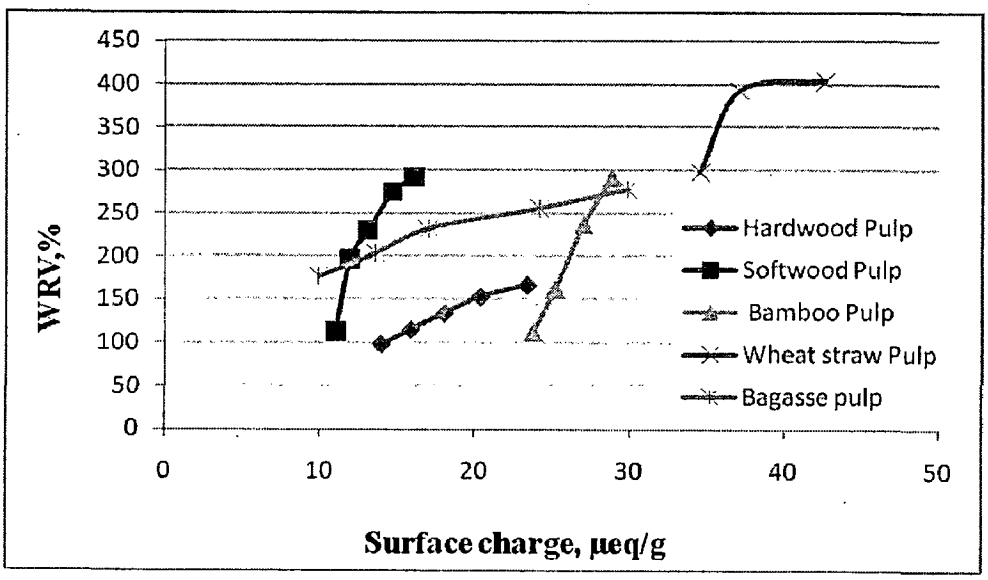

Fig. 15 Effect of refining on comparison of water retention value and surface charge.

The water retention value of bleached wheat straw pulp is higher than hardwood, softwood bamboo and bagasse pulp which shows that the fibrillation of fibres is more in this case. Wheat straw pulp has very high retention values as compared to other pulp samples.

WRV data is generally used in the measurement of water content as a percentage of oven dry weight. Results describe the higher initial beaten fibres has the higher water retention value. Also it is observed that WRV for wheat straw pulp is higher than other pulp samples.

Wheat straw > Baggase > Softwood > Bamboo > Hardwood

Also beating increases the pulp drainage resistance increased due to an increased in surface area (mainly fines formation). Internal fibrillation increases the fibre swelling and flexibility by loosening the cell wall structure and external fibrillation increases the outer surface of fibres.

4.5 The effect of refining on Classification of fibres through Bauer Mcnett Classifier

Table 9 gives us the actual amounts of fibres get used on wire part and the fines content in pulp. The fibres are collected on different mesh size like +16, +30, +50, +100, +200 and -200 meshes are treated as fines. Fig. 16 depicts Classification of different wood and non wood pulp fibres at different beaten and unbeaten levels.

***Table 9** Classification of fibers through Bauer McNett Classifier*

	Wheat straw, %		**Softwood, %**		**Hardwood,%**		**Bamboo, %**		**Baggase,%**	
Screen opening(mm)	**32.8 ^{0}SR**	**39.9 ^{0}SR**	**12.83 ^{0}SR**	**38.95 ^{0}SR**	**14.03 ^{0}SR**	**42.88 ^{0}SR**	**11.66 ^{0}SR**	**38.02 ^{0}SR**	**30.39 ^{0}SR**	**38.02 ^{0}SR**
1.189(+16)	...	...	51.5	21.5	...	...	56.3	56.4	...	...
0.595(+30)	2.56	1.78	33.5	33.5	10.4	0.45	8.2	3	19.6	19.8
0.297(+50)	39.91	37.95	2.14	18.14	42.1	49.8	20	25.6	29.6	26
0.149(+100)	19.11	11.51	2.9	11.5	24.5	12.5	5.8	4.5	14.45	10.7
0.074(+200)	14.78	9.54	...	...	7.3	17.86	...	...	19.15	20.5
Fines	23.64	39.22	9.96	15.36	15.7	19.39	9.7	10.5	17.2	23

For wheat straw the amount of fibres collected through +30 mesh at 32.8°SR is 2.56% which is very high as compared to wheat straw at 39.9 °SR. also the fibres at +200 mesh at 39.9 °SR is more than 28 °SR. The amount of fines increases at 39.9 °SR. In case of softwood and bamboo the amount of fibres at +16 meshes is reduced by great difference. In this case also, the fines content decreases with Schopper riegler values. At 39.9°SR and 38.02 °SR, wheat straw and baggase shows the nearly same amount of fines. This shows that raw material has itself great impact on drainage of fibres. It is observed in Literature survey that the burst factor and tensile strength of original stock were consistently higher than those of any individual fractions. The tear strength factor, on other hand, is highest in the coarse fraction and decrease successively to finer fraction.

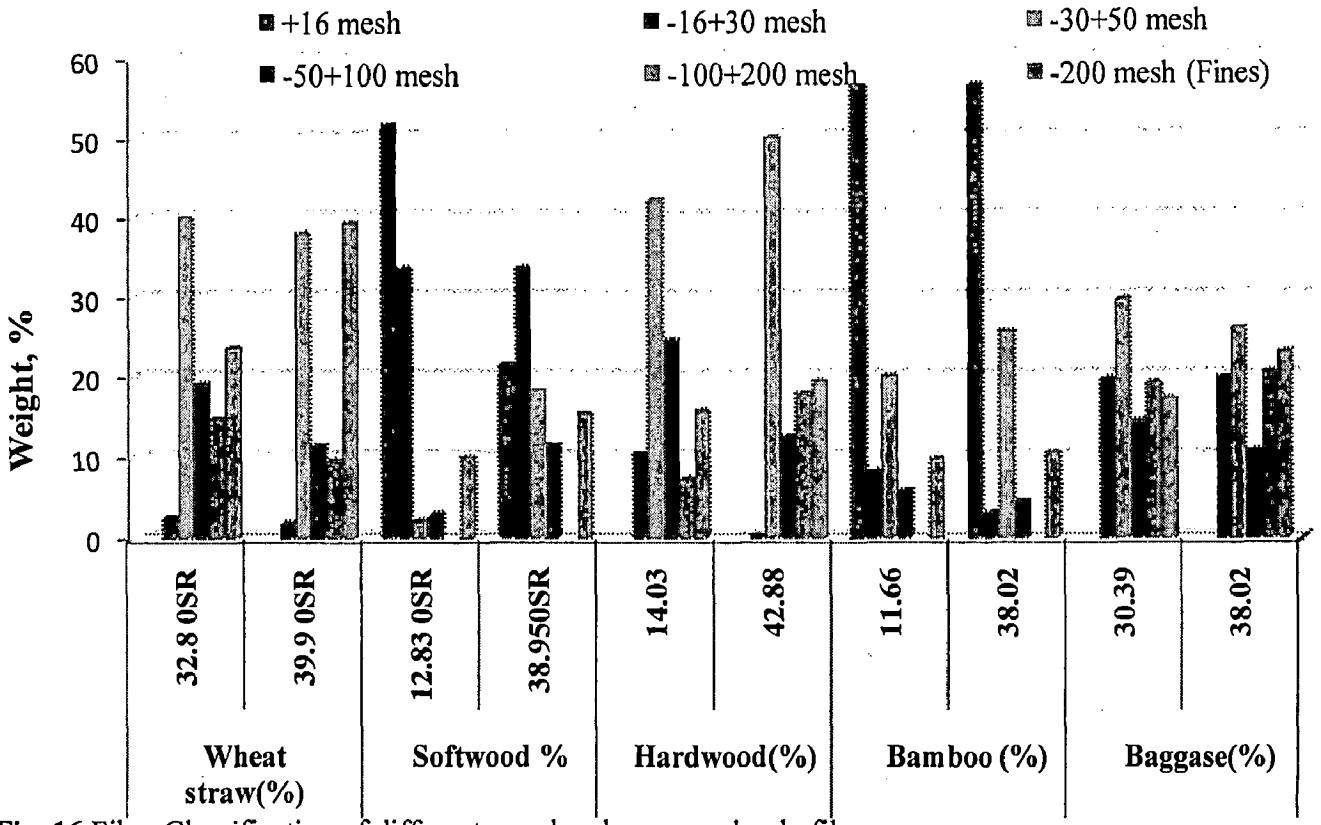

Fig. 16 Fibre Classification of different wood and non wood pulp fibres

The above figure shows the amount of fibres pass through the respected apertures. The fibre classification shows the quantity retained on 30 mesh screen (R_{30}); passed 30 mesh, retained 50 mesh (P_{30}/R_{50}); etc. The amount of fibres is varying for every size of aperture. The amount of fibres passes through 0.595mm screen opening as in case of hardwood R_{30} is 10.4%, in case of softwood R30 is 51.5 %, in case of baggase R_{30} is 19.6 % and in case of wheat straw R_{30} is 2.56%. It has been observed that on second stage beating the amount of fibres were rapidly passed through the same aperture and retained on later screen openings which ultimately lead to increase in amount of fines. Increase in amount of fines increases the drainage resistance of fibres. As increase in amount of fines increases the swelling of pulp which result in increases the specific volume and specific surface area of fibres. The maximum amount of fibres are collected on R_{50} mesh having opening as 0.297 mm. Amount of fines increases in case of 32.8°SR and 38.02 °SR. in all pulp samples which shows their fibrillation and cutting action. In case of wheat straw the drainage time is also high which shows wheat straw has some adverse effect compared to other pulps.

4.6 The effect of refining on paper properties

In Table 10 the strength properties (tensile index, breaking length, tear index, burst index and double fold values) of the handmade sheet made from British sheet former are compared as a function of CSF with revolutions as parameter.

Table 10 Comparison of Paper properties at various PFI Revolutions and freeness level

Pulp	PFI Revolutions, Nos.	Freeness, ml CSF	Drainage Time, sec	Tensile index, Nm/g	Tear index, mN m^2/g	Burst index, KPa.m^2/g	Double Fold, Nos.
Hard wood	0	670	12	12.13	8.30	2.06	25
	1000	540	13	17.06	9.07	3.37	27
	2000	460	14	20.32	8.87	5.58	30
	3000	370	15	27.19	8.81	5.81	33
	4000	290	16	32.46	8.68	6.74	36
Softwood	0	690	8	10.54	16.84	2.22	148
	2000	610	9	32.15	18.25	3.10	163
	3000	500	10	38.75	16.53	5.48	171
	4000	460	11	50.33	15.49	6.58	184
	5000	330	12	55.47	13.87	7.37	192
Bamboo	0	710	9	11.69	18.60	1.64	178
	2000	560	10	18.56	16.99	4.58	182
	4000	440	11	27.41	15.57	6.56	197
	5000	340	13	34.19	12.84	8.25	221
Wheat straw	0	400	21	30.85	5.36	4.57	32
	500	320	25	34.24	6.05	4.90	37
	1000	260	29	36.96	5.10	5.58	45
Bagasse	0	430	19	45.93	4.74	2.30	21
	1000	390	21	49.3o	5.39	3.14	22
	1500	340	24	52.59	5.05	3.60	24
	2000	270	26	55.13	4.74	3.75	27
	2500	225	28	58.88	4.65	4.29	34

4.6.1 The effect of refining drainage time

The Table 10 indicates that the drainage time required for fibres is varying from basic raw material; also the beating of fibres enhances its behaviour. The above table shows that wheat straw pulp and bagasse pulp are requiring more time as compared to hardwood, softwood and bamboo though their measured freeness is same. This may be due to the beating of wheat straw pulp is difficult as compared to other pulp samples. Also the water retention value of hardwood is low which shows the swelling of fibres is less as compared to others. Softwood

is drained very rapidly comparing to others. Fig. 17 shows different drainage characteristics at various freeness levels.

Drainage can be characterised as Wheat Straw > Baggase > Hardwood > Softwood.

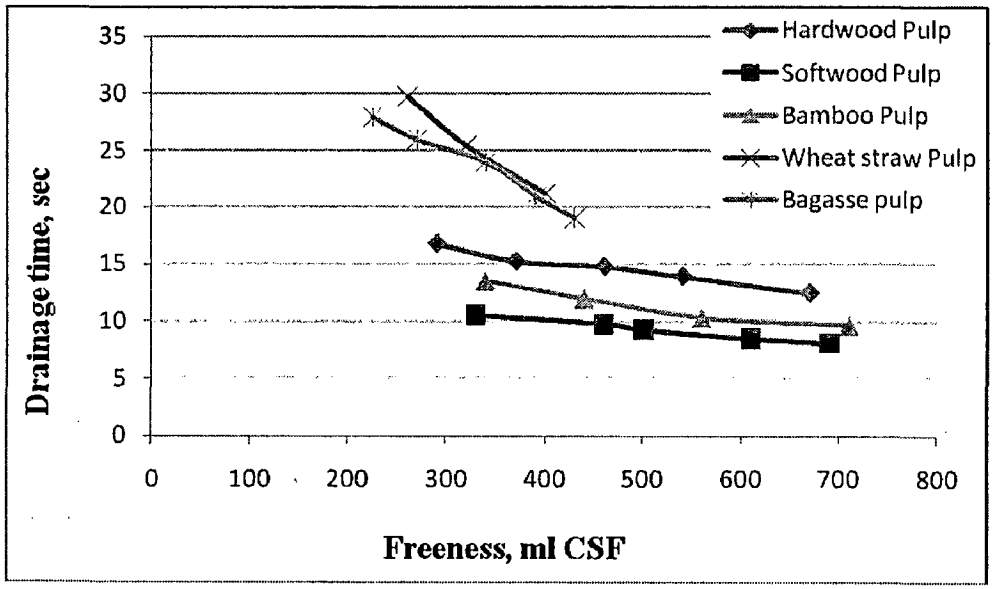

Figure 17 Characterization of drainage time at various freeness levels.

4.6.2 The effect of refining on tensile index

The Table 10 shows characterization of different parameters at various freeness levels and revolutions. Fig. 18 shows the effect of refining on tensile index of beating pulps. According to different beating pulps the tensile index is increases and at freeness levels the tensile index is decreased.

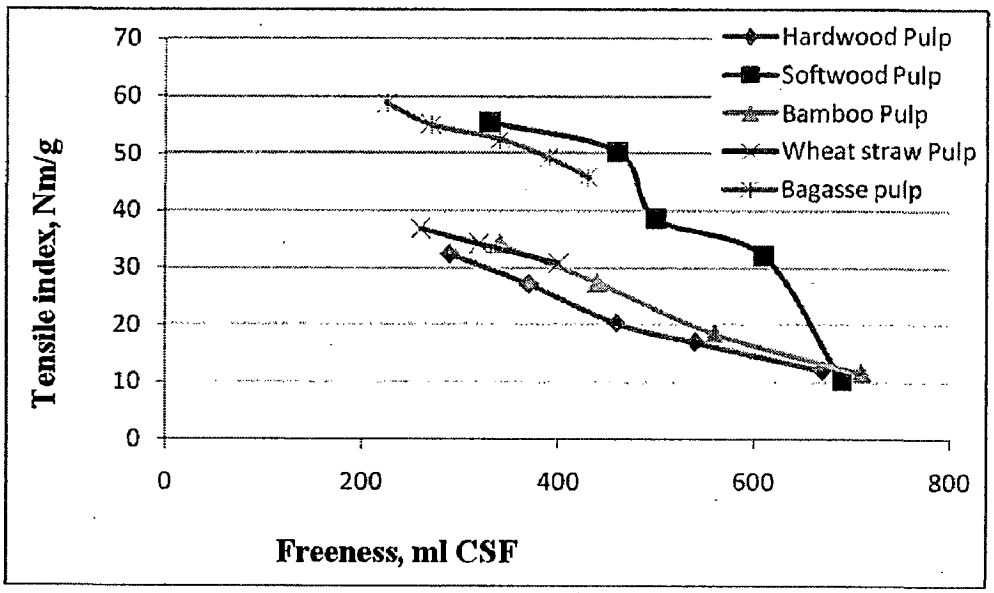

Fig. 18 Effect of refining on tensile index at various freeness levels.

4.6.3 The effect of refining on tear index

The Table 10 shows characterization of different parameters at various freeness levels and revolutions. In case of tear index initially for breaking of fibre to fibre bonds the tear strength requirement is high. As the beating increases the fibre-fibre bonds get broke which result in requirement of less tear strength as it is shown in fig. 19 it is declined.

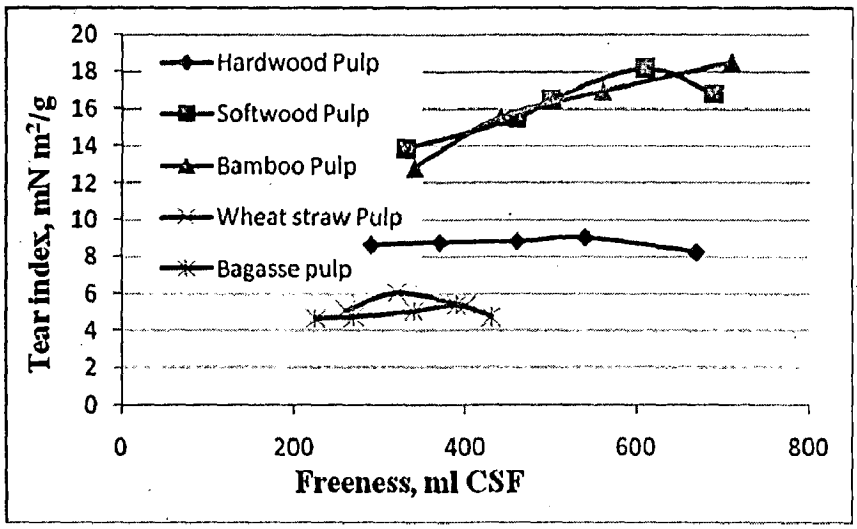

Fig. 19 Effect of refining on tear index at various freeness levels.

4.6.4 The effect of refining on burst index

The Table 10 shows characterization of different parameters at various freeness levels and revolutions. In fig. 20 shows the effect of refining on burst strength of beating pulps. According to different beating pulps the burst index is increases and at freeness levels the burst index is decreased.

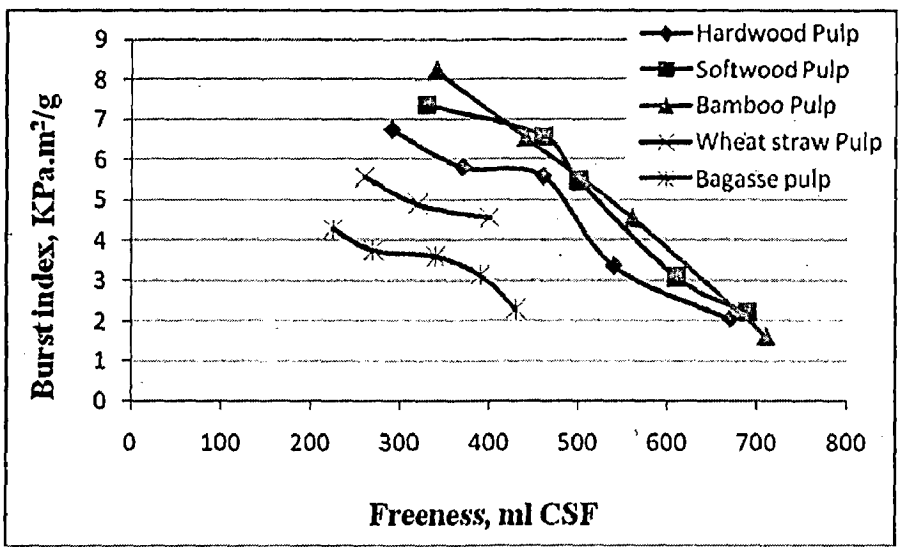

Fig. 20 Effect of refining on burst index at various freeness levels.

4.6.5 The effect of refining on folding endurance

The Table 10 shows characterization of different parameters at various freeness levels and revolutions. In fig. 21 shows the effect of refining on folding endurance of beating pulps. According to different beating pulps the folding endurance is slightly increases and at freeness levels the folding endurance is decreased.

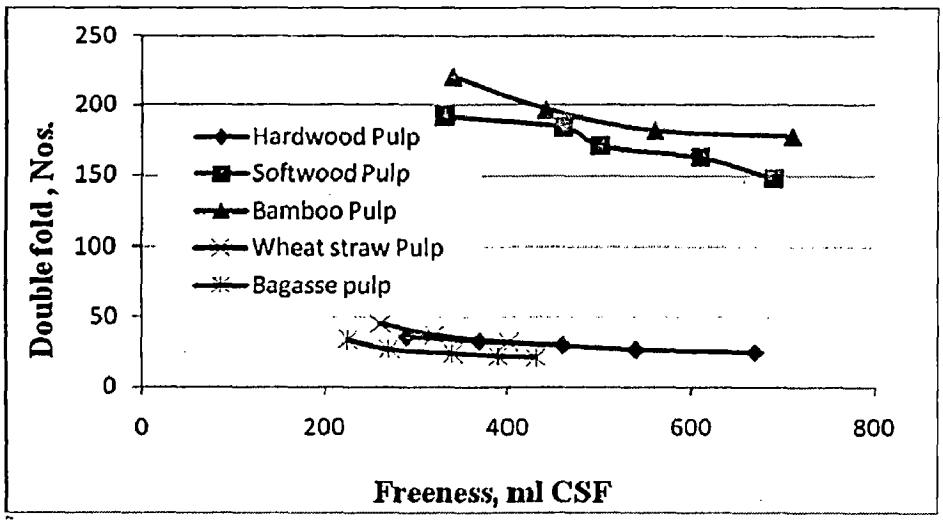

Fig. 21 Effect of refining on double fold no. at various freeness levels.

The pulps which are high in hemicelluloses beat more rapidly than those low in hemicelluloses. High hemi cellulosic content produces paper that is stronger in burst and tensile strength. This is consistent with the concept that the highly hydrophilic hemicelluloses absorb water, thereby causing fibre to swell and become flexible; the swelling results in weakening of bonds between fibrils, facilating fibrillation under mechanical treatment.

4.5 Statistical Interpretation of data

Based on the experimental data obtained from the laboratory are analysed from graphs and then subjected to statistical regression analysis. Least square techniques have been used. For simplicity linear regressions have been tried. Some important univariate linear regressions equations are developed. However, some are found to be distinctly linear whereas some possess slight nonlinear characteristics. Predicted data from regression models are plotted against experimental values in various graphs and percentage errors have been determined.

$$\text{Percentage error} = \frac{\text{Experimental value - Model predicted value}}{\text{Experimental value}} \times 100$$

These regression models along with the maximum and minimum percentage error are depicted in following Table 11.

***Table 11** Various Regression equations and coefficients, R^2 as a function of different parameters.*

Pulp	Parameters	Functions	Regression equations	R^2
Hard wood (Eucalyptus)	Freeness, ml CSF	Revolutions, Nos.	y = -0.093x + 652.000	R^2 = 0.99
	Surface charge, μeq/g	Freeness, ml CSF	y = -0.0245x + 29.799	R^2 = 0.97
	Sp. surface area, m^2/g	Freeness, ml CSF	y = -0.0061x + 5.5266	R^2 = 0.99
	Specific volume,cm^3/g	Freeness, ml CSF	y = -0.0042x + 6.7539	R^2 = 0.96
	WRV,%	Freeness, ml CSF	y = -0.1868x + 220.77	R^2 = 0.99
	Drainage Time, sec	Freeness, ml CSF	y = -0.0106x + 19.577	R^2 = 0.97
	Tensile index, Nm/g	Freeness, ml CSF	y = -0.0539x + 46.958	R^2 = 0.97
	Tear index, mN m2/g	Freeness, ml CSF	y = -0.0007x + 9.0784	R^2 = 0.13
	Burst index, KPa.m2/g	Freeness, ml CSF	y = -0.0127x + 10.624	R^2 = 0.94
	Double fold, Nos.	Freeness, ml CSF	y = -0.0296x + 44.001	R^2 = 0.97
Softwood	Freeness, ml CSF	Revolutions, Nos.	y = -0.0245x + 29.799	R^2 = 0.97
	Surface charge, μeq/g	Freeness, ml CSF	y = -0.0145x + 20.904	R^2 = 0.96
	Sp. surface area, m^2/g	Freeness, ml CSF	y = -0.0005x + 1.0363	R^2 = 0.93
	Specific volume,cm^3/g	Freeness, ml CSF	y = -0.0031x + 6.1444	R^2 = 0.96
	WRV,%	Freeness, ml CSF	y = -0.4864x + 473.26	R^2 = 0.89
	Drainage Time, sec	Freeness, ml CSF	y = -0.0069x + 12.835	R^2 = 0.99
	Tensile index, Nm/g	Freeness, ml CSF	y = -0.1203x + 99.774	R^2 = 0.89
	Tear index, mN m2/g	Freeness, ml CSF	y = 0.01x + 11.008	R^2 = 0.72
	Burst index, KPa.m2/g	Freeness, ml CSF	y = -0.0156x + 13.006	R^2 = 0.94
	Double fold, Nos.	Freeness, ml CSF	y = -0.1219x + 234.73	R^2 = 0.95
Bamboo	Freeness, ml CSF	Revolutions, Nos.	y = -0.0717x + 709.66	R^2 = 0.99
	Surface charge, μeq/g	Freeness, ml CSF	y = -0.0135x + 33.117	R^2 = 0.97
	Sp. surface area, m^2/g	Freeness, ml CSF	y = -0.0042x + 4.2687	R^2 = 0.90
	Specific volume,cm^3/g	Freeness, ml CSF	y = -0.0075x + 8.71	R^2 = 0.94
	WRV,%	Freeness, ml CSF	y = -0.4935x + 454.32	R^2 = 0.98
	Drainage Time, sec	Freeness, ml CSF	y = -0.0106x + 16.784	R^2 = 0.93
	Tensile index, Nm/g	Freeness, ml CSF	y = -0.0615x + 54.506	R^2 = 0.98
	Tear index, mN m2/g	Freeness, ml CSF	y = 0.0149x + 8.3617	R^2 = 0.94
	Burst index, KPa.m2/g	Freeness, ml CSF	y = -0.0178x + 14.377	R^2 = 0.99
	Double fold, Nos.	Freeness, ml CSF	y = -0.1128x + 252.32	R^2 = 0.85
Wheat straw	Freeness, ml CSF	Revolutions, Nos.	y = -0.14x + 396.67	R^2 = 0.99
	Surface charge, μeq/g	Freeness, ml CSF	y = -0.0563x + 56.506	R^2 = 0.91
	Sp. surface area, m^2/g	Freeness, ml CSF	y = -0.0005x + 1.9945	R^2 = 0.97
	Specific volume,cm^3/g	Freeness, ml CSF	y = -0.0107x + 7.3962	R^2 = 0.99
	WRV,%	Freeness, ml CSF	y = -0.7811x + 620.55	R^2 = 0.88
	Drainage Time, sec	Freeness, ml CSF	y = -0.0605x + 45.223	R^2 = 0.99
	Tensile index, Nm/g	Freeness, ml CSF	y = -0.0436x + 48.251	R^2 = 0.99
	Tear index, mN m2/g	Freeness, ml CSF	y = 0.0013x + 5.0818	R^2 = 0.03
	Burst index, KPa.m2/g	Freeness, ml CSF	y = -0.007x + 7.3188	R^2 = 0.92
	Double fold, Nos.	Freeness, ml CSF	y = -0.0912x + 67.797	R^2 = 0.95
Bagasse	Freeness, ml CSF	Revolutions, Nos.	y = -0.085x + 450	R^2 = 0.94
	Surface charge, μeq/g	Freeness, ml CSF	y = -0.0952x + 50.441	R^2 = 0.99
	Sp. surface area, m^2/g	Freeness, ml CSF	y = -0.0067x + 5.1287	R^2 = 0.93
	Specific volume,cm^3/g	Freeness, ml CSF	y = -0.0081x + 6.6949	R^2 = 0.97
	WRV,%	Freeness, ml CSF	y = -0.5479x + 406.55	R^2 = 0.94
	Drainage Time, sec	Freeness, ml CSF	y = -0.043x + 37.836	R^2 = 0.98
	Tensile index, Nm/g	Freeness, ml CSF	y = -0.0592x + 71.945	R^2 = 0.98
	Tear index, mN m2/g	Freeness, ml CSF	y = 0.0018x + 4.3224	R^2 = 0.24
	Burst index, KPa.m2/g	Freeness, ml CSF	y = 0.0008x + 2.3365	R^2 = 0.98
	Double fold, Nos.	Freeness, ml CSF	y = -0.0585x + 44.978	R^2 = 0.88

It is evident that all the regression models developed are very accurate as the regression coefficients, R2 are close to unity (on an average above 0.98) and the percentage error does not exceed in any case ± 7%. The model predicted data and the experimental data are compared in various graphs. A few of them are shown as typical examples. The detailed graphs are given in Appendix F. The plots between models predicted data and experimental data show an excellent agreement between them. Therefore statistical predictions are claimed to be very good and reproducible with a reasonable degree of accuracy permitted in engineering estimates. Therefore the statistical regression can be used reliably for analysis purposes.

From the detailed analysis of data and their interpretation it can be certainly stated without any doubt that the surface area of fibres plays an important role in the bonding of the fibres, but tear index of model predictions and regression coefficients for wood and non wood pulps are not close to unity. A large fibre surface area provided higher fibre surface charge and more areas for Fibre–Fibre contacts and, subsequently, more number of bonds is developed between fibres. The experimental results also showed strong linear correlations between the surface charge and the hand sheets properties.

4.5.1 Regression Model Diagnostics

Model adequacy checking is an important part of the data analysis procedure. This is equally important in building regression models. The residual plots that we used with designed experiments should always be examined for a regression model. In general, it is always necessary to (1) examine the fitted model to ensure that it provides an adequate approximation to the true system and (2) verify that none of the least squares regression assumptions are violated. The regression model will probably give poor or misleading results unless it is an adequate fit.

In addition to residual plots, there are other mode diagnostics that are frequently useful in regression [22].

The model adequacy can be easily investigated by the examination of residuals. The residuals for the two-factor factorial model are

Residual, e_{ij} = Experimental value (Y_{ij}) – Model predicted value ($\hat{Y}_{ij}$).

Plotting the residuals in freeness data collection is helpful in detecting correlation between the residuals

Plot of Residuals versus fitting Values (Model Predicted Value):

If the model is correct and if the assumptions are satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted values $\hat{Y}_{ij}$.

Residuals plots between residuals and predicted values are attempted. The detailed graphs are given in Appendix F.

4.5.2 Correlation and regression [21]:

The experimental conditions are used for the measurement of the standards and for the test (unknown) sample, the concentration of the test sample may be determined from the calibration curve by graphical interpolation.

Two statistical procedures should be applied to a calibration curve:

(a) Test whether the graph is linear or in the form of a curve.

(b) Find the best straight line (or curve) through the data points.

The linear relationship between two variables X_i and Y_i, use correlation coefficient r:

$$r = \frac{n\sum X_i Y_i - \sum X_i \sum Y_i}{\{[n\sum X_i^2 - (\sum X_i)^2][n\sum Y_i^2 - (\sum Y_i)^2]\}^{1/2}}$$

Where n is the number of data points.

The value of r must be lie between +1 and -1; the nearer is to ±1, the greater the probability that a definite linear relationship exists between the variables X and Y; values close to +1 indicate positive correlation and values close to -1 indicate negative correlation. Values of r tha tend towards zero indicte that V are not linearly related (they may be related in a non-linear fashion).

Although the correlation coefficient, r would easily be calculated with the aid of a modern calculator or computer package.

4.5.3 Linear regression (the method of least squares) [21]:

The linear relationship has been shown to have a high probability by the value of the correlation coefficient r, and then the best straight line through the data points has to be estimated. To evaluate the best straight line by linear regression (the method of least squares) is as follows:

The equation of a straight line is

$Y = mX + C$

Where Y is the depended variables, is plotted as a result of changing X, the independent variables.

To obtain the regression line Y on X, the slope *m* of the line and the intercept C on the Y-axis are given by the following equations:

$$\text{Slope, } m = \frac{n\sum XiYi - \sum Xi\sum Yi}{n\sum Xi^2 - (\sum Xi)^2}$$

and

$$\text{Intercept, } C = \bar{X} - \bar{y}$$

Where $\bar{x}$ is the mean of all values of X and $\bar{y}$ is the mean of all values of Y.

4.5.4 Errors in the slope and intercept [21]:

The determination of errors in the slope *m* and the intercept *C* of the regression line may be calculated in the following manner. First, the term $S_{y/x}$ must be evaluated from the following equation:

$$S_{y/x} = \sqrt{\frac{\sum(Yi - \hat{Y})2}{(n-2)}}$$

The $\hat{Y}$ values are obtained from the calculated regression line for given values of X.

$$\text{The standard deviation of the slope } S_m = \frac{Sy/x}{\sqrt{\sum(Xi - \bar{X})2}}$$

$$\text{The standard deviation of the intercept } S_c = S_{y/x}\sqrt{\frac{\sum Xi^2}{n\sum(Xi - \bar{X})^2}}$$

4.5.5 Errors in the estimate of concentration [21]:

The estimation of the error in the concentration determined by the use of the regression line involved the following expression:

$$S_{xc} = \frac{Sy/x}{m}\left[\left[1 + \frac{\cdot}{n} + \frac{(Y_0 - \bar{Y})^2}{m^2\sum(X - \bar{X})^2}\right]^{1/2}\right.$$

Where Y_0 is the value of Y from which the concentration X_c is to be evaluated and where S_{xc} is the standard deviation of X_c. The detailed data are depicted in following Appendix F.

CHAPTER 5 CONCLUSIONS

From the detailed analysis of data and their interpretation through graphs, the following noteworthy conclusions can be made:

- Refining operation increases surface charge, specific surface area and specific volume of fibres, but did not change the total fibre charge or in other words, the total fibre charge is not affected by refining, but the fibre surface charge increases with the degree of refining.
- The increases in specific surface area as well as the increase in surface charge of the fibres are apparently relevant to the improvement of fibre–fibre bonding.
- The water retention values give the extent of degree of swelling and it is found that the softwood has high water retention values and in case of agro residues wheat straw has high water retention values.
- Bauer McNett classifier has been studied very carefully and it's observed the behaviour of fibre is varying widely in quantity of fibres though they were beaten at sane freeness values. Fibre distribution of softwood pulp at 30 meshes is high.
- In overall comparison it is found that softwood fibres drained very easily. Also the baggase fibres showing some results as it shows good tensile strength and tear strength properties but still required high drainage time.
- Bamboo pulp shows good burst strength and high number of double folds.
- The strength properties of agro residues were showing the same behaviour as woody fibers but in this case also it has been observed that baggase has high strength properties the bonding of fibres is high compared to wheat straw.
- The strength properties of paper made from modified fibres are greatly improved, but the introduction of carboxyl groups also increases the swelling of the fibres.
- The experimental results also showed strong linear correlations between the surface charge and the hand sheets properties.
- The regression equation agrees excellently with the model predicted data with regression coefficient close to unity.
- Model adequacy checking is good relation between residuals and model predicted values with coefficient of determination close to unity.
- The parametric relationship between regression coefficient (R^2) and coefficient of determination (r^2) is same as in all cases.

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CHAPTER 7 APPENDICES

APPENDIX A

Determination of fibre surface charge by polyelectrolyte titration is as follows:

For unbeaten bleached hardwood pulp

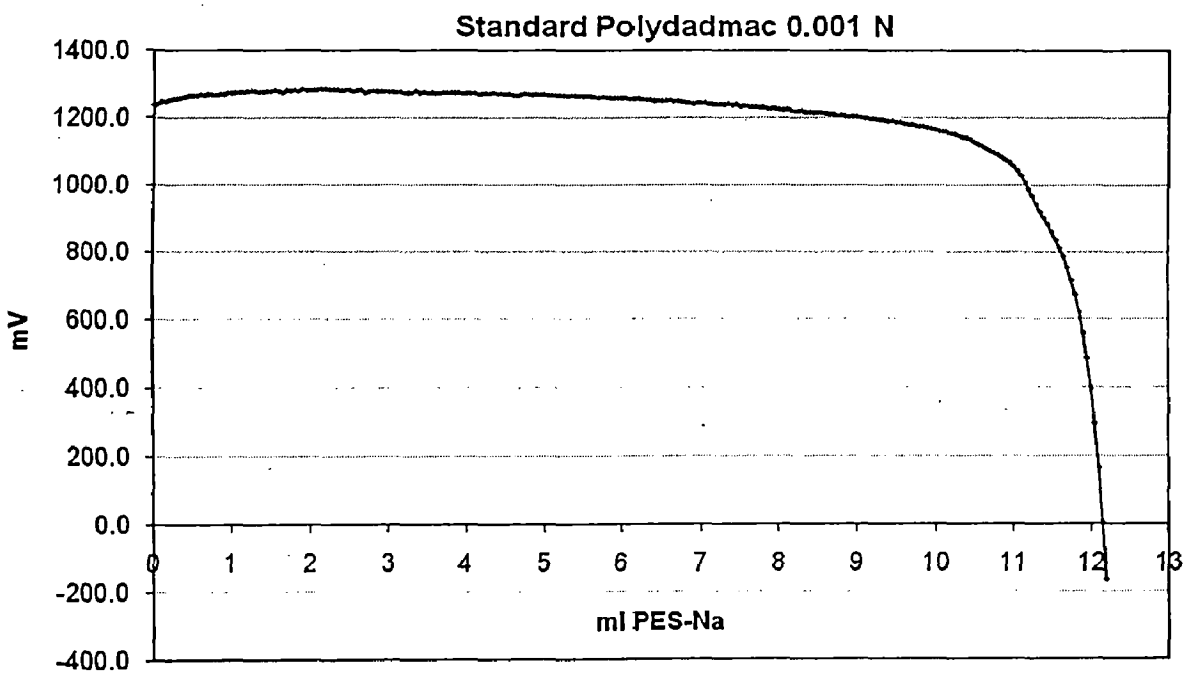

Fig. 22 Streaming potential (mV) versus sodium polyethylenesulphate (Na-PES, ml) at unbeaten bleached hardwood pulp

The specific charge density of the sample is calculated by the formula below:

$$q = \frac{(V_p - V_b) \times c \times 1000}{w}$$

Where

q is the specific charge density (mmol/kg),
V_p is the volume of titrant used for pulp (ml),
V_b is the volume of titrant used for blank (ml),
c is the concentration of titrant (mol/l), and
w is the solid content of pulp (g).

APPENDIX B

Determination of total charge by Conductometric titration is as follows:

For unbeaten bleached hardwood pulp

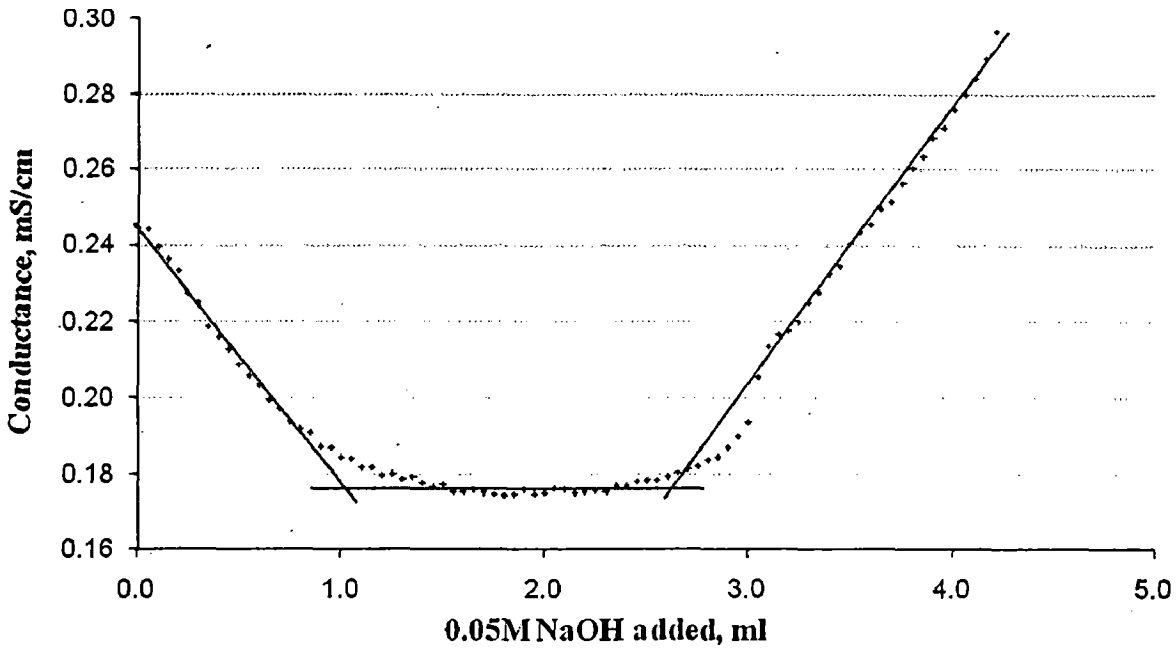

Fig. 23 Conductance versus 0.05 M NaOH added, ml at unbeaten bleached hardwood pulp

The Total charge of the sample is calculated by the formula below:

$$\text{Total charge} = \frac{(V_2 - V_1) * c}{m}$$

Where

$V_2 - V_1$: Difference between the charges of the 0.1 M NaOH added, ml and the reacted 0.1 M NaOH added, ml indicates the charge amount neutralized in the sample.

c: Concentration of the titrant, i.e. here 0.1 M NaOH added, ml.

m: 0.5 g of the original sample are used for titration.

APPENDIX C

Determination of sp. surface area and sp. volume by permeability test is as follows:

Table 12 Calculation of specific surface area and specific volume for hardwood pulp

Pulp	Pressure Drop (ΔP), g/cm2	Rotameter Reading	Flow (q), cm3/min	ΔP/q	Pad Weight, W(g)	Permeation Resistance,	Pad Thickness, cm	Pad Area, A (cm^2)	Pad Density, g/cm3	$(C/RP)^{1/3}$ * 1000
Eucalyptus	6.5	145	15.8	0.411	7.89	337551330.8	3.4	28.27	0.082	0.624
	8	142	15.5	0.516	7.89	423787072.2	3.2	28.27	0.087	0.590
	9.5	138	15	0.634	7.89	520699619.8	3	28.27	0.093	0.563
	11	135	14.6	0.753	7.89	618433460.1	2.8	28.27	0.099	0.544
	13.5	131	14	0.964	7.89	791726235.7	2.6	28.27	0.107	0.513
	17	123	12.9	1.317	7.89	1081642586	2.4	28.27	0.116	0.475
	20	115	11.8	1.694	7.89	1391269962	2.2	28.27	0.126	0.450
	25	100	9.6	2.604	7.89	2138646388	2	28.27	0.139	0.402

Unbeaten hardwood	Slope	Intercept	b	b^3	k	kb^3	$1/kb^3$	Sp. surface area (Sw), cm^2/g	Sw, m^2/g	v, cm^3/g
	3.713	0.9159	0.0009	7.68E-10	5.55	4.26E-09	234510795.5	15313.74531	1.53	4.05

G 20020

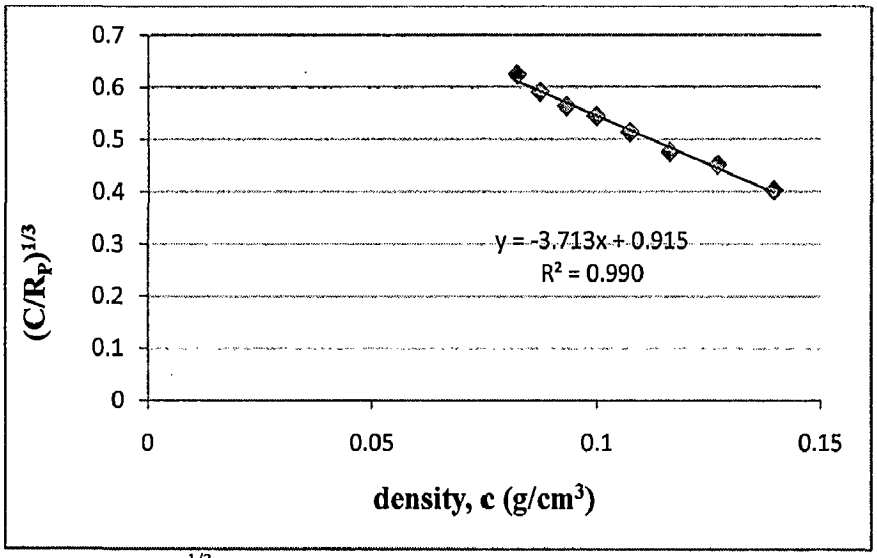

Fig. 24 $(C/R_p)^{1/3}$ versus density, c

APPENDIX D

Determination of water retention value by centrifuge method is as fallows:

For unbeaten bleached hardwood pulp

Pulp = 0.18 g

Water = 18 ml

Empty cylinder weight = 39.52 g

After centrifuge

At Speed-2400 No. and Time-30 min

(E.C + Pulp) weight = 39.858 g

Pulp weight = 39.858 – 39.52 = 0.338 g

After oven dry

(E.C + Pulp) weight = 39.681 g

Pulp weight =39.681 – 39.52 = 0.161 g

$$WRV = \frac{\text{wet weight} - \text{Dry weight}}{\text{Wet weight}} \times 100$$

$$WRV = \frac{0.338 - 0.161}{0.18} \times 100$$

WRV = 98.34 %.

APPENDIX E

Determination of hand sheet properties:

For unbeaten bleached hardwood pulp

- Strip weight = 1.32g
- gsm = 1.32× 50 = 66 g/m^2
- Thickness = 7.6 × 0.01 mm = 7.6 × 0.01 × 1000 μm = 76 μm
- Bulk = Thickness (mm) / gsm = 0.076 × 1000/66 = 1.15 m^3/g
- Tensile Strength = 1.35Kg/15 mm

  Breaking length = Tensile strength / gsm = T.S × 10^6 / (15 × gsm)

  = 1.35× 10^6 / (15 × 66) =1363.63 m

  Tensile index = B.L × 0.0089 = 1363.63 × 0.0089 = 12.13636364N.m/g
- Tear strength = 27.97 g.force

  Tear factor = 27.97 ×2/gsm ×100= 27.97 × 2/66 × 100 = 84.75

  Tear index = T.F × 0.098 = 84.75× 0.098 = 8.30 mN m^2/g
- Burst strength = 1.43 Kgf/cm^2

  Burst factor = B.S/67.9 × 1000 = 21.06

  Burst index = B.F × 0.098 = 21.06 × 0.098 = 2.06 KPa m^2/g
- Double fold = 25.

APPENDIX F

Statistical Interpretation of Data:

The model predicted data and the experimental data are compared in various graphs are as follows:

Example: Freeness Vs PFI Revolutions for bleached hardwood pulp

Regression equation and regression coefficient are

$y = -0.093x + 652$, $R^2 = 0.99$

$$\% \text{ Error} = \frac{\text{Experimental value} - \text{Model predicted value}}{\text{Experimental value}} \times 100$$

Table 13 The experimental value and model predicted values for bleached hardwood pulp at $y = -0.093x + 652$, $R^2 = 0.99$

Freeness, ml CSF (Y)	Revolutios, Nos. (X)	Model predicted data ($\hat{Y}$)	% Error	Residuals (e_{ij})
670	0	652	2.68	18
540	1000	559	-3.51	-19
460	2000	466	-1.30	-6
370	3000	373	-0.81	-3
290	4000	280	3.44	10

Fig-A depicts the relationships between the experimental value and model predicted values for hardwood pulp at Freeness (y) versus Revolutions(x): $y = -0.093x + 652$, $R^2 = 0.99$ are shown below:

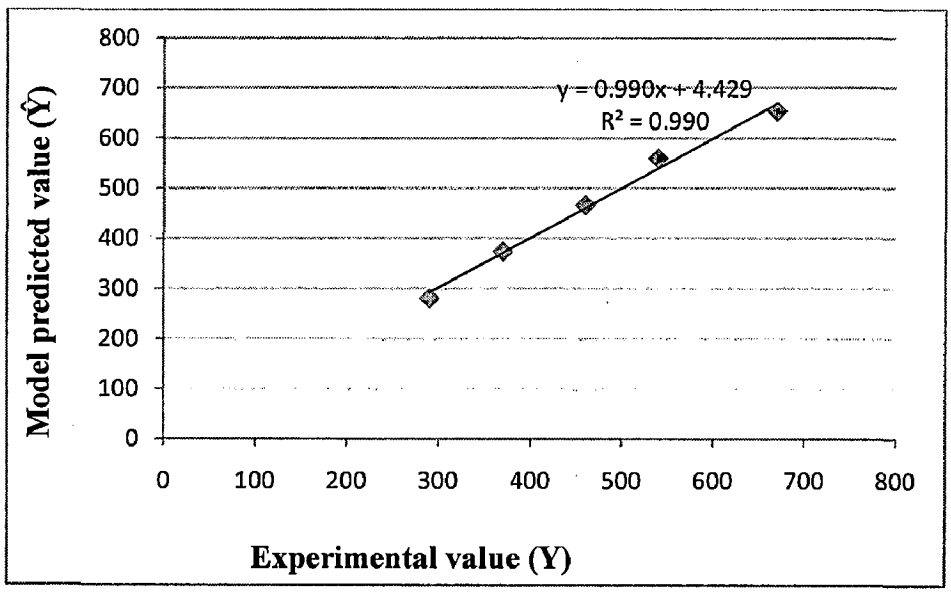

Fig. 25 The experimental value and model predicted values for hardwood pulp at Freeness (y) versus Revolutions(x): $y = -0.093x + 652$, $R^2 = 0.99$

It is evident from the plots that the predicted Vs experimental values agree to high degree of accuracy.

Plot of Residuals versus fitting Values (Model Predicted Value):

If the model is correct and ifthe assumptions are satisfied, the residuals should be structureless; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted values $\hat{Y}ij$.

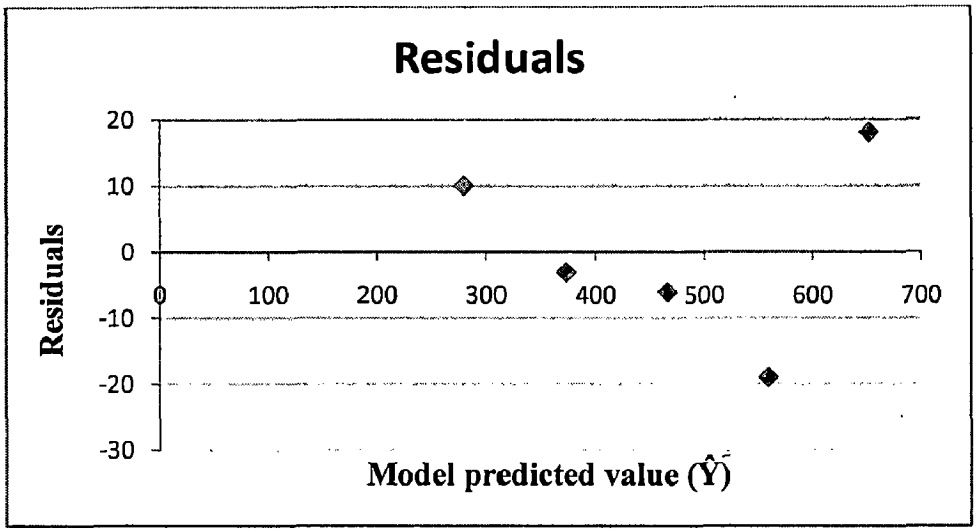

Fig. 26 Residuals Vs predicted values of freeness value at hardwood pulp.

Above figures have been drawn to examine the behaviour of the residuals as a function of predicted values of the above mentioned parameters. It is clear from figures that the residuals are almost distributed around zero. The best prediction is obtained for freeness in all cases, the surface charge will follow. Through the residuals for specific surface area and specific volume are not up to the level of accuracy of that for freeness, but still can be accepted for order of estimates, permitted by engineering calculations.

Correlation and regression

Table 14 *Calculation of correlation coefficient*

Freeness, ml CSF (Y_i)	**Revolutios, Nos.(X_i)**			
$\sum Y_i$	$\sum X_i$	$\sum X_i^2$	$\sum Y_i^2$	$\sum X_i Y_i$
670	0	0	448900	0
540	1000	1000000	291600	540000
460	2000	4000000	211600	920000
370	3000	9000000	136900	1110000
290	4000	16000000	84100	1160000
2330	**10000**	**30000000**	**1173100**	**3730000**

$\bar{x} = \sum X/n = 466$

$\bar{y} = \sum X/n = 2000$

$n \sum X_i Y_i = 18650000$

$\sum X_i \sum Y_i = 23300000$

$n \sum X_i^2 = 150000000$

$(\sum X_i)^2 = 100000000$

$n \sum Y_i^2 = 5865500$

$(\sum Y_i)^2 = 5428900$

$n \sum X_i Y_i - \sum Xi \sum Yi = -4650000$

$n \sum X_i^2 - (\sum X_i)^2 = 50000000$

$n \sum Y_i^2 - (\sum Y_i)^2 = 436600$

$\{[n \sum X_i^2 - (\sum X_i)^2] [n \sum Y_i^2 - (\sum Y_i)^2]\}^{1/2} = 4672258.554$

Correlation coefficient, r = -0.995236018

Coefficient of determination, $r^2 = 0.99059$.

Linear regression (the method of least squares):

The equation of a straight line is

$Y = mX + C$

Where Y, the depended variables, is plotted as a result of changing X, the independent variables.

To obtain the regression line Y on X, the slope *m* of the line and the intercept C on the Y-axis are given by the following equations:

Slope, $m = \frac{n \sum XiYi - \sum Xi \sum Yi}{n \sum Xi2 - (\sum Xi)2} = -0.093$

and

Intercept, $C = \bar{x} - \bar{y} = -1534$

Where $\bar{x}$ is the mean of all values of X and $\bar{y}$ is the mean of all values of Y.

Clearly, Y = -0.093X - 1534C

Errors in the slope and intercept:

The determination of errors in the slope *m* and the intercept *C* of the regression line may be calculated in the following manner. First, the term $S_{y/x}$ must be evaluated from the following equation:

$$S_{y/x} = \sqrt{\frac{\Sigma(Yi - \hat{Y})2}{(n-2)}} = 16.63329993$$

The $\hat{Y}$ values are obtained from the calculated regression line for given values of X.

The standard deviation of the slope $S_m = \frac{Sy/x}{\sqrt{\Sigma(Xi - \bar{X})2}} = 5.57408E\text{-}07$

The standard deviation of the intercept $S_c = S_{y/x} \sqrt{\frac{\Sigma Xi^2}{n\Sigma(Xi - \bar{X})^2}} = 0.001365365$

Errors in the estimate of concentration:

The estimation of the error in the concentration determined by the use of the regression line involved the following expression:

$$S_{xc} = \frac{S_{y/x}}{m}\left[\left[1 + \frac{1}{n} + \frac{(Y0 - \bar{y})^2}{m^2\Sigma(x - \bar{x})^2}\right]^{1/2} = \pm 195.924\right.$$

Where Y_0 is the value of Y from which the concentration X_c is to be evaluated and where S_{xc} is the standard deviation of X_c.

Table 15 The experimental value, model predicted value and residuals for bleached hardwood pulp at y = -0.02x + 29.79, R^2 = 0.97

surface charge, µeq/g	Freeness, ml CSF	Model predicted data ($\hat{Y}$)	% Error	Residuals (e_{ij})
14.01	670	13.384	4.46	0.626
15.94	540	16.569	-3.94	-0.629
18.11	460	18.529	-2.31	-0.419
20.43	370	20.734	-1.48	-0.304
23.35	290	22.694	2.80	0.656

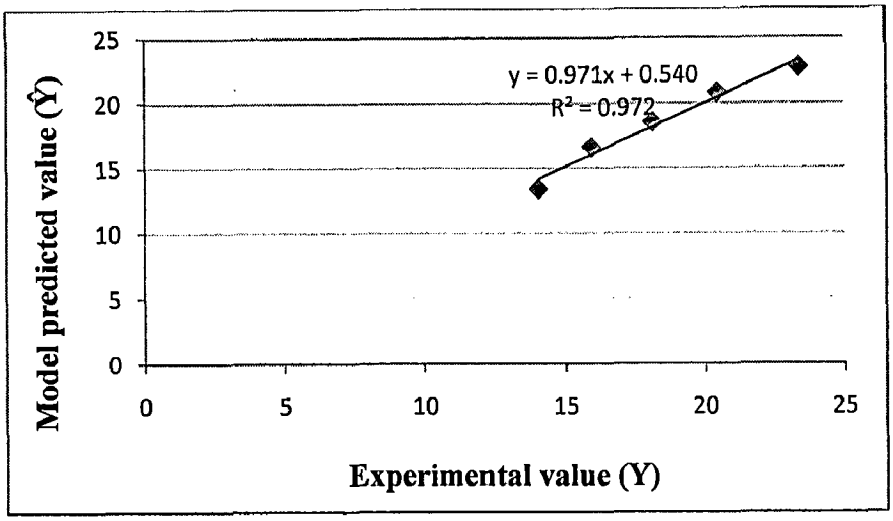

Fig. 27 The experimental value and model predicted values for bleached hardwood pulp at $y = -0.02x + 29.79$, $R^2 = 0.97$

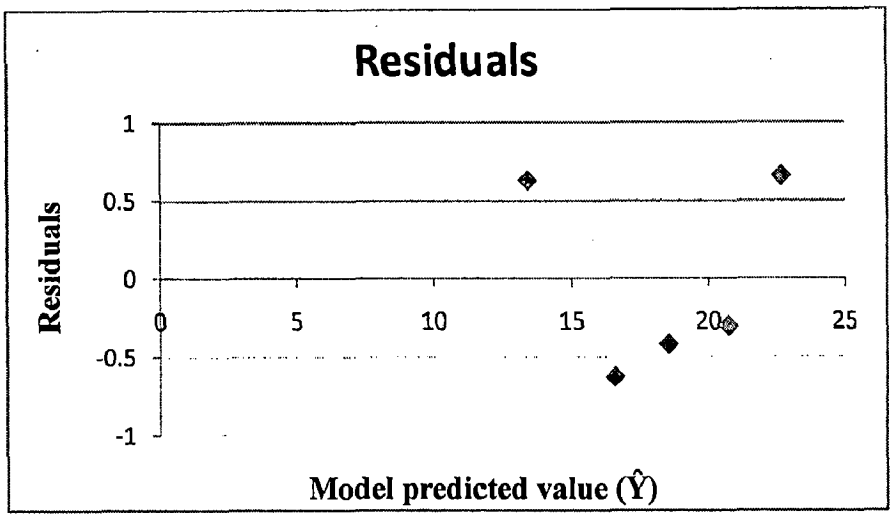

Fig. 28 The residuals and model predicted values for bleached hardwood pulp at $y = -0.02x + 29.79$, $R^2 = 0.97$

Table 16 *The experimental value, model predicted value and residuals for bleached hardwood pulp at* $y = -0.006x + 5.52$, $R^2 = 0.99$

S_w, m^2/g	Freeness, ml CSF	Model predicted data (Ŷ)	% Error	Residuals (e_{ij})
1.53	670	1.4396	5.90	0.0904
2.11	540	2.2326	-5.81	-0.1226
2.73	460	2.7206	0.34	0.0094
3.23	370	3.2696	-1.22	-0.0396
3.83	290	3.7576	1.89	0.0724

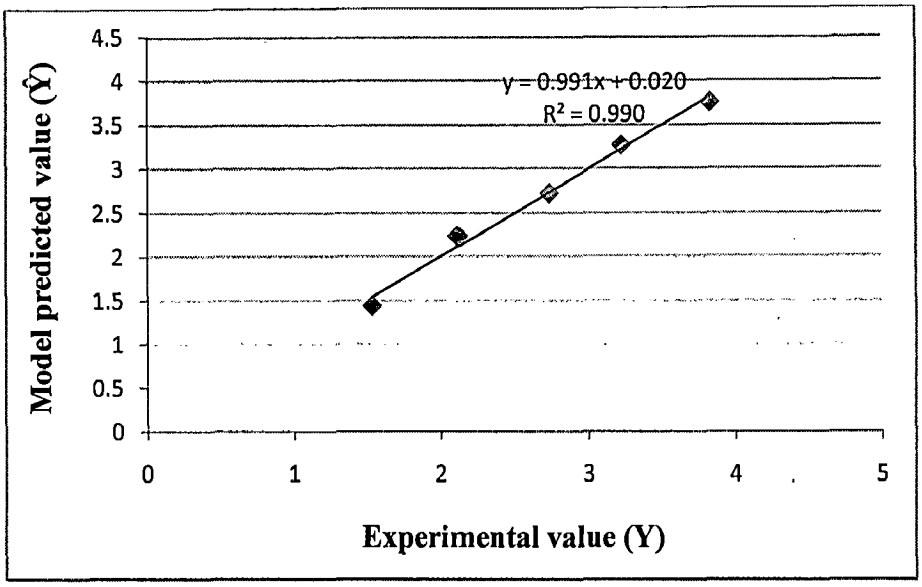

Fig. 29 The experimental value and model predicted values for bleached hardwood pulp at $y = -0.006x + 5.52$, $R^2 = 0.99$

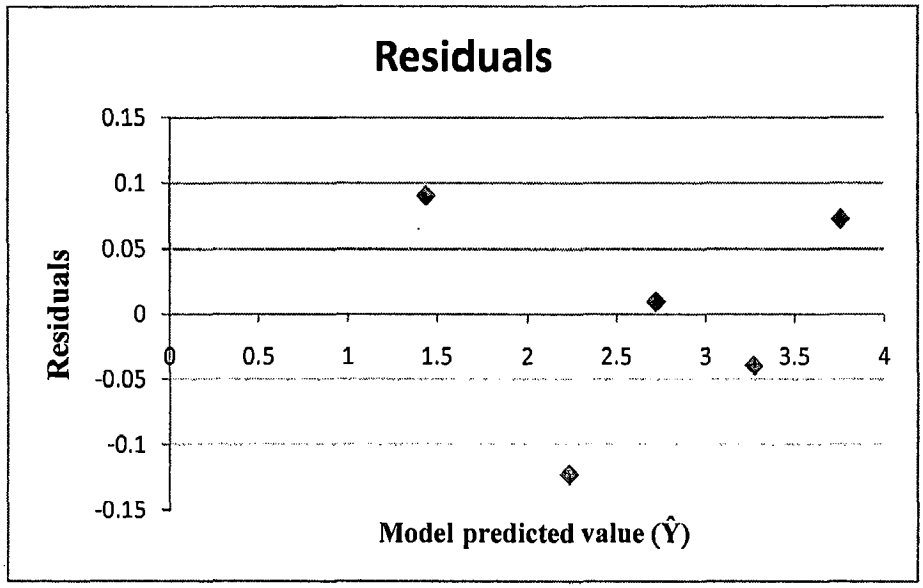

Fig. 30 The residuals and model predicted values for bleached hardwood pulp at $y = -0.006x + 5.52$, $R^2 = 0.99$

Table 17 *The experimental value, model predicted value and residuals for bleached hardwood pulp at* $y = -0.004x + 6.75$, $R^2 = 0.96$

v, cm^3/g	Freeness, ml CSF	Model predicted data ($\hat{Y}$)	% Error	Residuals (e_{ij})
4.05	670	3.9399	2.71	0.1101
4.36	540	4.4859	-2.88	-0.1259
4.7	460	4.8219	-2.593	-0.1219
5.16	370	5.1999	-0.77	-0.0399
5.65	290	5.5359	2.01	0.1141

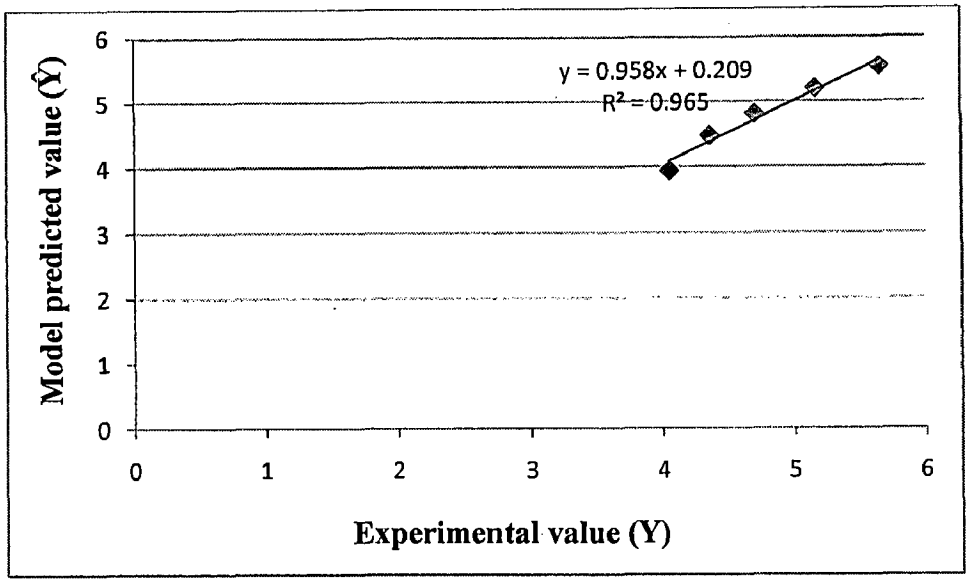

Fig. 31 The experimental value and model predicted values for bleached hardwood pulp at y = -0.004x + 6.75, $R^2 = 0.96$

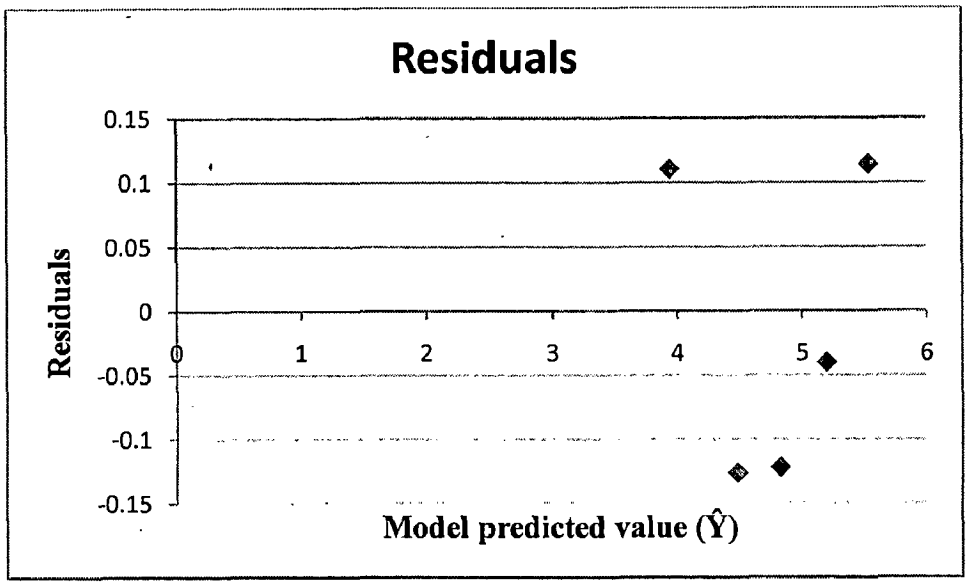

Fig. 32 The residuals and model predicted values for bleached hardwood pulp at at y = -0.004x + 6.75, $R^2 = 0.96$

Table 18 *The experimental value, model predicted value and residuals for bleached hardwood pulp at y = -0.18x + 220.7, $R^2 = 0.99$*

WRV,%	Freeness, ml CSF	Model predicted data (Ŷ)	% Error	Residuals (e_{ij})
98.34	670	95.614	2.77	2.726
115.56	540	119.898	-3.75	-4.338
134.45	460	134.842	-0.29	-0.392
153.34	370	151.654	1.09	1.686
167.01	290	166.598	0.24	0.412

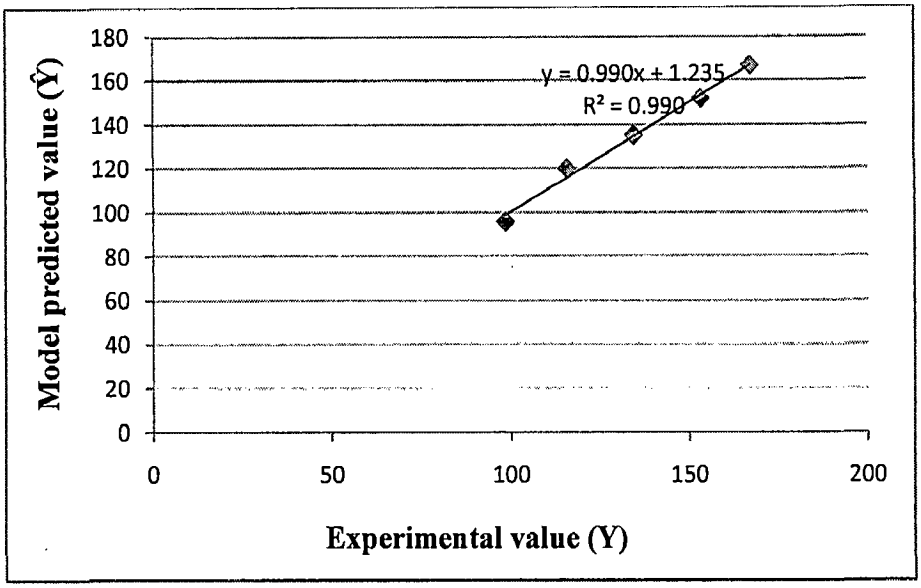

Fig. 33 The experimental value and model predicted values for bleached hardwood pulp at y = -0.18x + 220.7, R^2 = 0.99

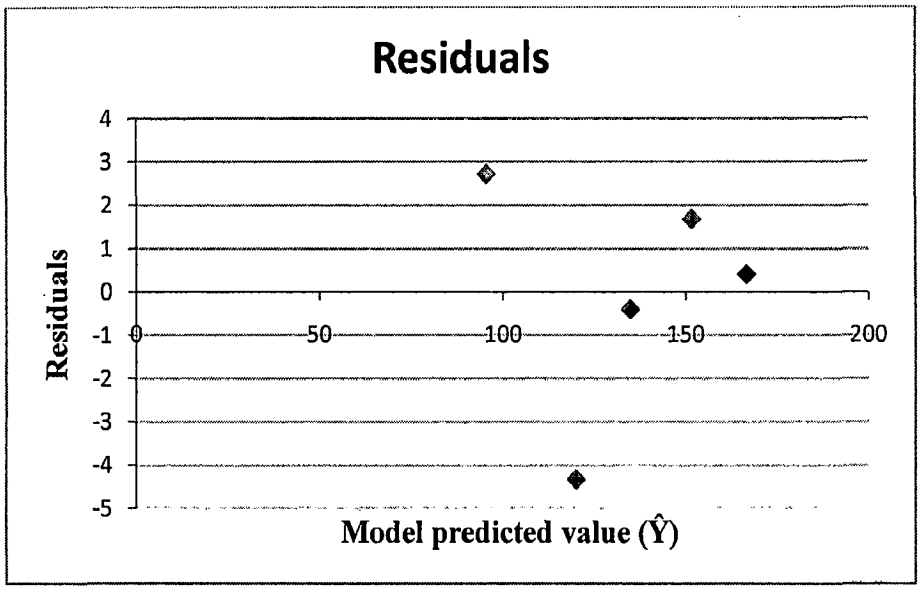

Fig. 34 The residuals and model predicted values for bleached hardwood pulp at y = -0.18x + 220.7, R^2 = 0.99

Table 19 *The experimental value, model predicted value and residuals for bleached hardwood pulp at y = -0.01x + 19.57, R^2 = 0.97*

Drainage Time, sec	Freeness, ml CSF	Model predicted data (Ŷ)	% Error	Residuals (e_{ij})
12.48	670	12.475	0.04	0.005
13.92	540	13.853	0.48	0.067
14.77	460	14.701	0.46	0.069
15.23	370	15.655	-2.79	-0.425
16.77	290	16.503	1.59	0.267

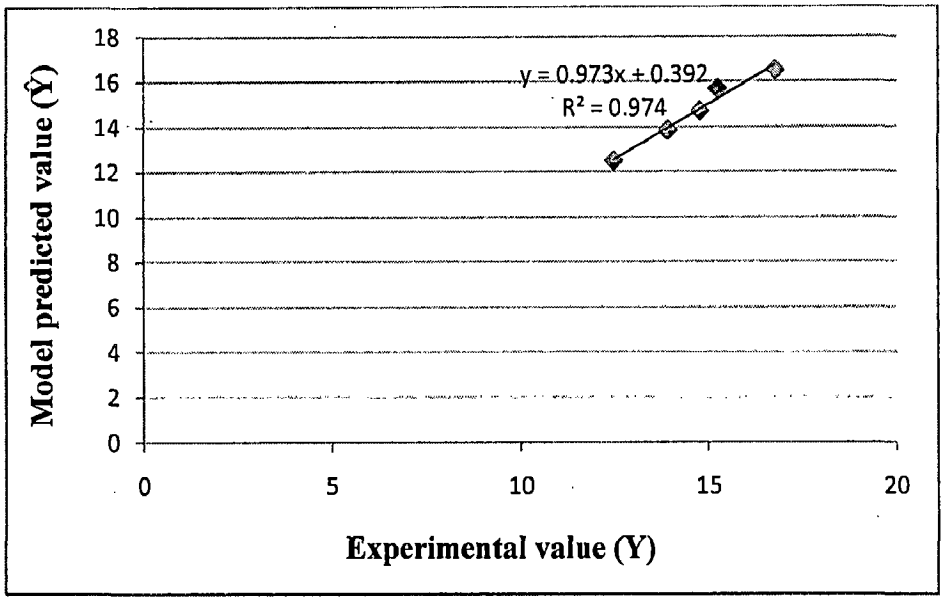

Fig. 35 The experimental value and model predicted values for bleached hardwood pulp at $y = -0.01x + 19.57$, $R^2 = 0.97$

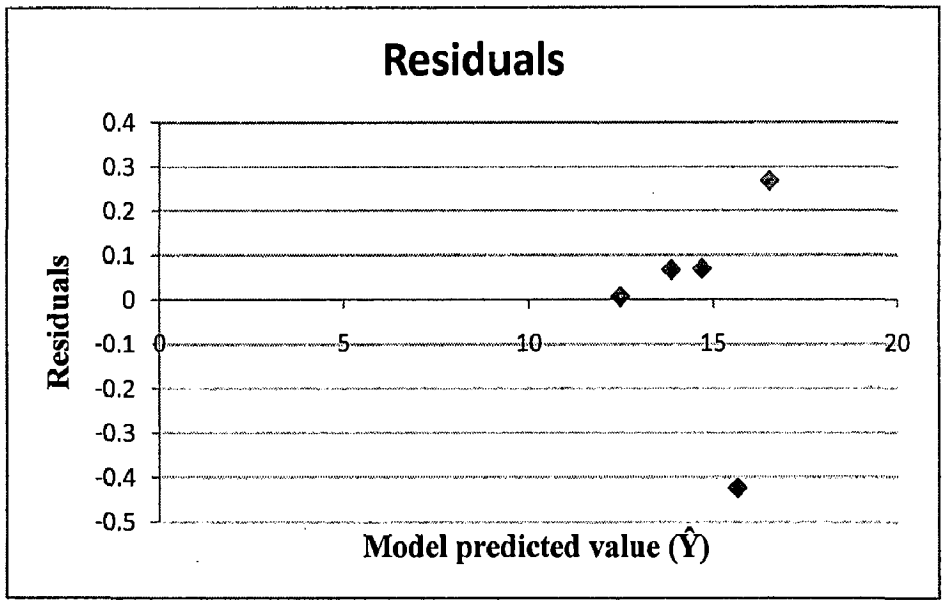

Fig. 36 The residuals and model predicted values for bleached hardwood pulp at $y = -0.01x + 19.57$, $R^2 = 0.97$

Table 20 *The experimental value, model predicted value and residuals for bleached hardwood pulp at* $y = -0.05x + 46.95$, $R^2 = 0.97$

Tensile index, Nm/g	Freeness, ml CSF	Model predicted data (Ŷ)	% Error	Residuals (e_{ij})
12.13	670	10.845	10.59	1.285
17.06	540	17.852	-4.64	-0.792
20.32	460	22.164	-9.07	-1.844
27.19	370	27.015	0.64	0.175
32.46	290	31.327	3.49	1.133

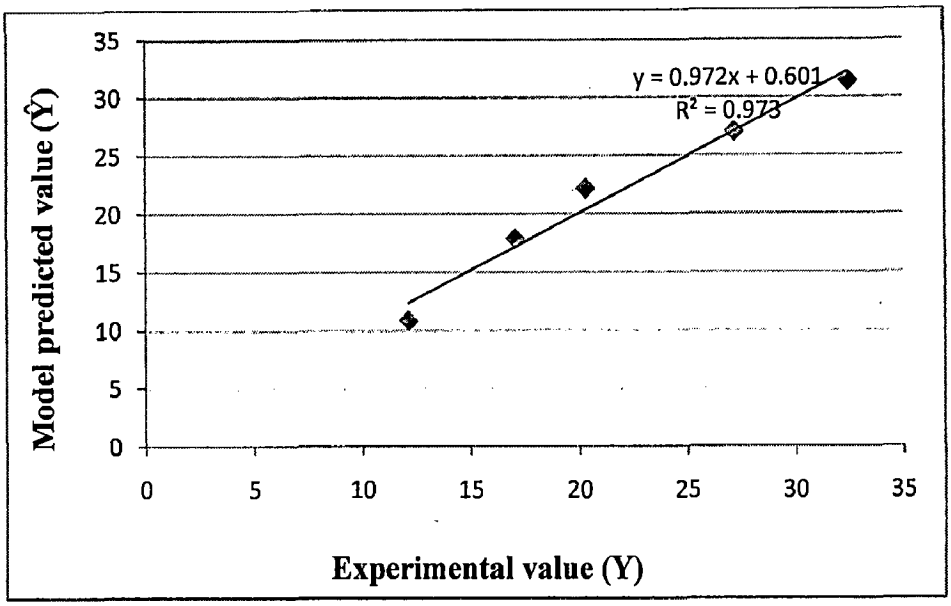

Fig. 37 The residuals and model predicted values for bleached hardwood pulp at y = -0.05x + 46.95, $R^2 = 0.97$

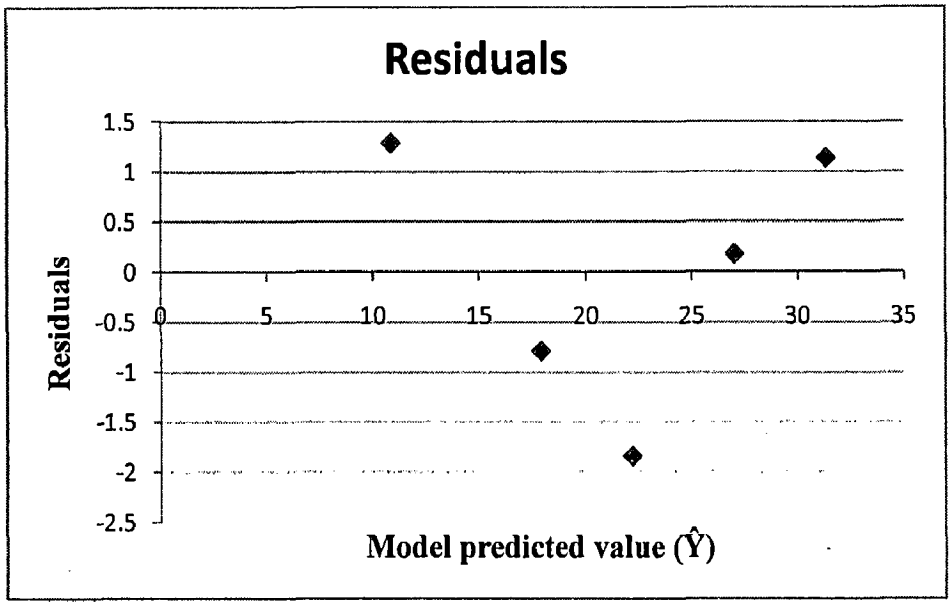

Fig. 38 The experimental value and model predicted values at y = -0.05x + 46.95, $R^2 = 0.97$

Table 21 *The experimental value, model predicted value and residuals for bleached hardwood pulp at* $y = -0.01x + 10.62$, $R^2 = 0.94$

Burst index, KPa.m2/g	Freeness, ml CSF	Model predicted data (Ŷ)	% Error	Residuals (e_{ij})
2.06	670	2.115	-2.66	-0.055
3.37	540	3.766	-11.75	-0.396
5.58	460	4.782	14.30	0.798
5.81	370	5.925	-1.97	-0.115
6.74	290	6.941	-2.98	-0.201

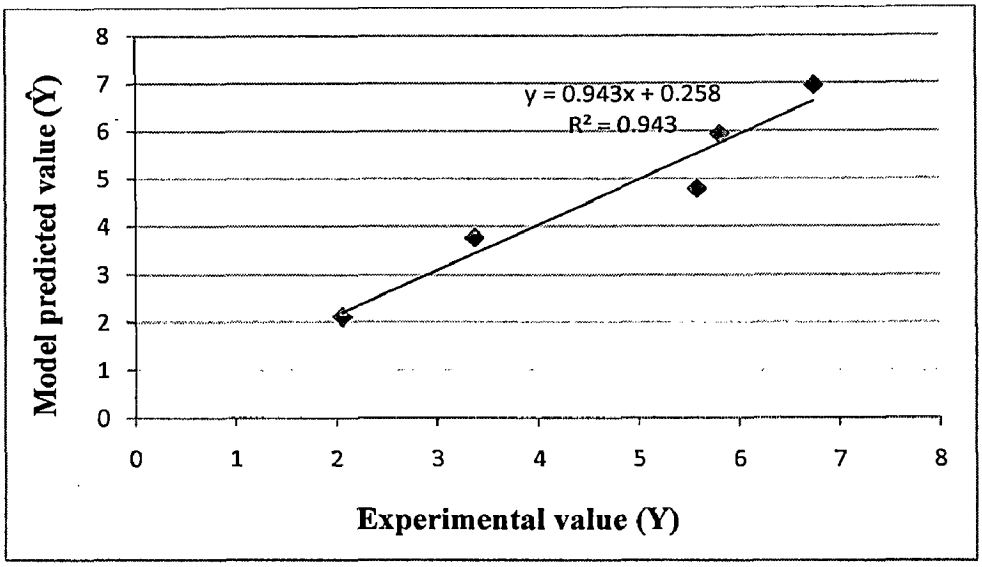

Fig. 39 The experimental value and model predicted values for bleached hardwood pulp at $y = -0.01x + 10.62$, $R^2 = 0.94$

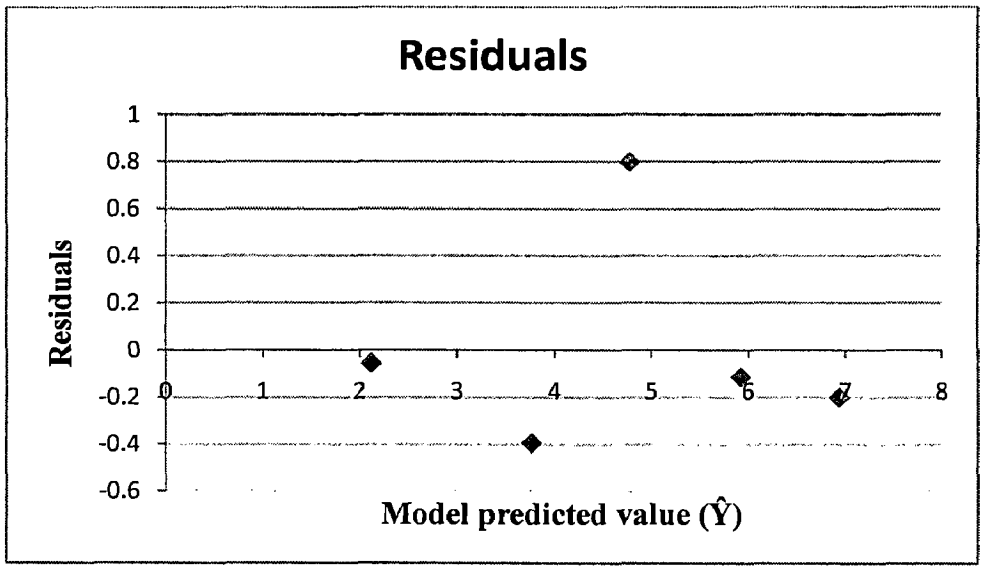

Fig. 40 The residuals and model predicted values for bleached hardwood pulp at $y = -0.01x + 10.62$, $R^2 = 0.9$

Table 22 *The experimental value, model predicted value and residuals for bleached hardwood pulp at* $y = -0.029x + 44$, $R^2 = 0.97$

Folding endurance	Freeness, ml CSF	Model predicted data (Ŷ)	% Error	Residuals (e_{ij})
25	670	24.169	3.32	0.831
27	540	28.017	-3.76	-1.017
30	460	30.385	-1.28	-0.385
33	370	33.049	-0.14	-0.049
36	290	35.417	1.61	0.583

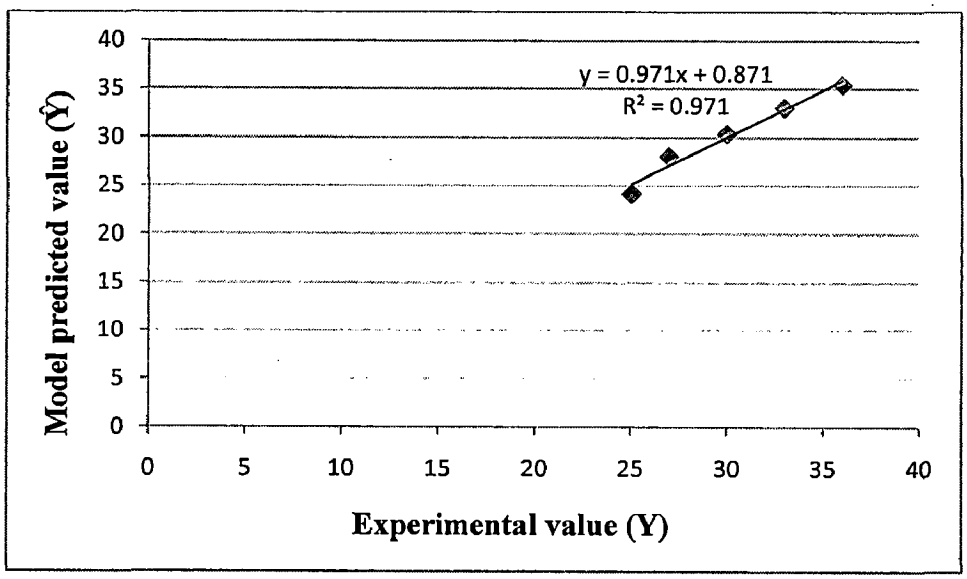

Fig. 41 The experimental value and model predicted values for bleached hardwood pulp at $y = -0.029x + 44$, $R^2 = 0.97$

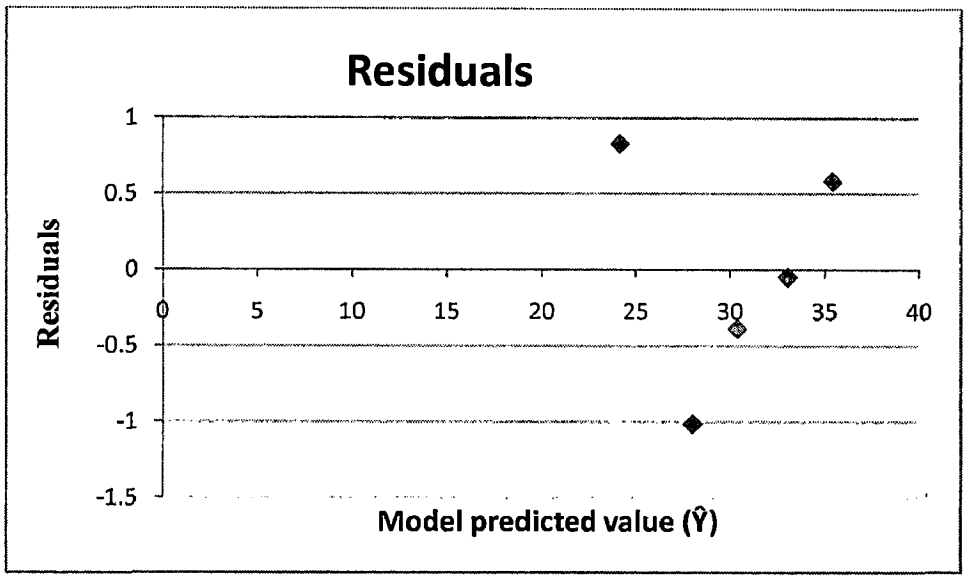

Fig. 42 The residuals and model predicted values for bleached hardwood pulp at $y = -0.029x + 44$, $R^2 = 0.97$